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THE INSTITUTE OF PETROLEUM.

An Ordinary General Meeting of the Institute of Petroleum was held at Manson House, 26, Portland Place, London, W.1, on Wednesday, February 11, 1948. Mr T. Dewhurst (Past-President) was in the Chair.

The Minutes of the preceding Ordinary Meeting, held on January 14, 1948, were read, confirmed, and signed.

The General Secretary (Mr F. H. Coe) announced the names of those elected to membership of the Institute by the Council. He also announced the subject of the next General Meeting.

The Chairman, introducing Dr N. J. M. Taverne (Bataafsche Petroleum Maatschappij) and inviting him to present his paper on aerial photography, said: Aerial photography was established in the first world war and was used subsequently for many purposes—civil engineering projects, the development of mines and land, forestry, archæology, etc.; very remarkable discoveries were made in the realm of archæology.

In the 1920's the aeroplane was much used for petroleum exploration in the United States, and in 1925–26 the Sarawak Oilfields Ltd., surveyed 1300 square miles in Sarawak, using aeroplanes of the Aerial Survey Company. Since those early days this method of exploration has evolved until in recent years (at least in all areas where solid geology is exposed) photo-geology has become the first weapon in the armoury of the petroleum geologist. A geologist on the ground is very much like a fly on the picture, whereas from an aeroplane he can see and photograph the whole picture. Wherever formations of different composition and hardness have been exposed to the agents of denudation, those tools of earth sculpture have chiselled out the lineaments of the geological structure.

Long ago I was familiar with a number of domes, the summits of which had been mapped in great detail. When those areas were photographed, the resulting photo-geological maps were somewhat in the nature of a revelation, for they showed clearly, not only the dome summits, but their general setting and their relationship to neighbouring structures. The microscope had been replaced by binoculars.

The publication of methods and results has lagged far behind developments and achievements in photo-geology. The year 1933 was most fruitful, because in that year we had two papers read at our meetings on the subject and several papers were read and discussed at the first World Petroleum Congress. Since then we have had only one short paper on this important subject. It follows, therefore, that Dr Taverne's paper will fill a very big gap in our records and will bring members up-to-date on a subject of the first importance.

We are doubly fortunate in that Dr Taverne is a master of his subject. For about thirty years he has been engaged in geological exploration; as early as 1925 he was awarded a Doctorate in Science for a thesis which was partly based on observations and photographs from the air. He has held a number of responsible posts and has carried out geological work in many countries, notably Java, Sumatra, New Guinea, Papua, and the United

States. Part of the time he spent in the United States was devoted to experimental work on aerial photography.

He is now to give us the results of his experience and researches, and I have very much pleasure in inviting him to present his paper.

DR TAVERNE then presented the following paper:

AERIAL PHOTOGRAPHY AND EXPLORATION FOR OIL.

By Dr N. J. M. TAVERNE.*

SYNOPSIS.

This paper is not offered as a complete treatise on the application of aerial photography in prospecting for oil, but is designed to give a short summary of the historical development of air mapping and to present a review of those principles of photogrammetry which are of particular interest to the interpreter of aerial photographs and also to discuss some important methods and applications of photography from the air in exploration for oil.

HISTORICAL REVIEW.

AIR MAPPING depends upon many inventions the most significant of which are photography, stereoscopy, photogrammetry and last, but not least, the aeroplane.

The origin of the principle of photography goes as far back as the recording in 350 B.C. by Aristotle of the optical projection of the round image of the sun through a square aperture.

Many centuries later the camera obscura made its appearance when Leonardo da Vinci, that amazing scientist, engineer, aeroplane designer, and artist, discovered its secrets as early as the second half of the fifteenth or the beginning of the sixteenth century.

In 1802 Thomas Wedgewood succeeded in printing by contact silhouettes of images on leather, sensitized with silver nitrate, and introduced an important new element in the reproduction of images.

It was not, however, until many years later—between 1835 and 1837—that reproduction of images was further developed by Daguerre, who evolved a method of direct photography on a silver plate superficially converted into silver iodide and fixation of the latent image by mercury vapour.

The construction of the first stereoscope was another step forward in photographic mapping. Such an instrument without lenses was introduced in 1834 by Elliot. In 1838 Wheatstone designed the first mirror stereoscope and Brewster followed in 1844 with the construction of a prismatic stereoscope.

Photography and stereoscopy being available, Laussedat in 1852 built the first apparatus for terrestrial photogrammetry. Pairs of overlapping photographs of a landscape were taken with a photo-theodolite at two stations, the distance between which had been measured with chain or transit. By this method the co-ordinates or location of each point appearing on the overlapping parts of the two photographs could be calculated.

* Bataafsche Petroleum Maatschappij.

The next step, almost simultaneously developed with the terrestrial photo-theodolite, was photography from the air instead of from the ground. These aerial pictures were made from kites and later, in 1858, also from balloons. In 1893 Adams, in the U.S.A., took out a patent for air mapping from a balloon. Incidentally, in his application he indicated for the first time the principle of aerial triangulation.

Meanwhile further development of the stereoscope had given rise to the construction of stereophotogrammetric instruments for the drawing of contour maps from pairs of overlapping photographs.

In the stereocomparator constructed by Pulfrich in 1901 the co-ordinates as well as the differences in altitude of separate points were measured. In 1909 Orel developed the stereo-autograph, an instrument for making contour maps with the help of an operator specially trained in observation of stereoscopic images.

After the first world war photography from aeroplanes made rapid progress and navigational instruments for photo-flying were greatly improved. Special aerial cameras of the single as well as the multiple-lens type were designed; moreover, new supersensitive emulsions for photographic plates and films came into use. New methods for aerial triangulation were worked out and improved. The air survey gradually superseded many ground surveys, particularly in more or less unknown areas where topographic maps were either lacking or of poor quality.

In the United Kingdom, the U.S.A., Canada, the Netherlands, and many other countries, commercial companies and also government agencies such as the Geodetic Survey of Canada, and the Soil Conservation Service of the U.S.A. specialized in aerial photography and carried out extensive aerial surveys. Originally these surveys were undertaken with a view to making topographic maps either in the form of line maps or as aerial mosaics. Later the air maps were also used for general reconnaissance of unknown areas and occasionally for forest inventories (Canada).

Soon the indispensability of finding new methods of geodetic control was felt. Ingenious means of aerial triangulation were discovered limiting the errors which are inherent to maps derived from aerial pictures.

Later it became evident that the air-photographs apart from bringing to light a wealth of topographic details in open country also showed geological features which were of great interest to the explorer for oil and other minerals. Field geologists found that in countries with scarce vegetation aerial pictures were not only of great help for plotting geological ground observations, but also could be used for elucidating structural and sometimes even stratigraphical problems. Shortly after the first world war, for instance, oil geologists, in the U.S.A. made frequent use of single air-photographs or of mosaics for geological mapping, particularly if a general reconnaissance of an area was required; for detail work the scale of the photographs often proved too small. Not until later was the study of overlapping photographs introduced with the help of a small pocket stereoscope.

Up to the early 'thirties the use of air pictures for geological purposes was mainly limited to non-tropical countries. It was generally thought that the thick tropical jungle would conceal the geological features.

In 1934 the Bataafsche Petroleum Maatschappij (B.P.M.) studied the

possibility of demarcation of the boundaries of newly acquired concessions in Sumatra on aerial photographs, with a view to eliminating the costly surveying and marking of these boundaries on the ground.

As the Government proved willing to accept this new method of demarcation, provided the aerial maps fulfilled certain specifications (*e.g.*, that they were properly compiled in accordance with modern photogrammetric methods), a systematic aerial survey of these concessions covering approximately 1000 square miles was carried out.* During the study of these photographs it became clear that the principal structural features of anticlines and synclines were clearly detectable through a mirror stereoscope equipped with magnifying glasses, in spite of the presence of a continuous cover of tropical vegetation, the top of which reached a height of approximately 100 ft above the ground. This discovery induced the geological department of the B.P.M. to propose a systematic aerial survey, not only for topographical, but also for geological purposes, of a new concession of 40,000 square miles in Netherlands New Guinea where conditions as far as vegetation is concerned are very much similar to those of Sumatra.

This aerial survey was carried out in 1936–37 jointly by the B.P.M., Standard-Vacuum, and Standard of California. This expedition is believed to be the first exploration venture in a jungle-covered tropical country where photo-geological interpretation was applied, covering a vast area, prior to geological ground reconnaissance. Methods similar to those applied during this expedition have since been used by the Shell group and other oil companies in tropical areas of South America, Burma, British India, and also in more open countries such as occur in Australia, Portuguese Timor, Madoera (near Java), etc.

Before the second world war investigations were made in the U.S.A. with special aerofilms, sensitive to infra-red rays, as well as tests with rather primitive methods of aerial colour photography. These tests, however, yielded only meagre results.

Some Geometric Characteristics of Aerial Photographs.

Scale.

A map is an orthographic projection of a small part of the earth and is supposed to have a uniform scale. On an aerial photograph the scale varies due to differences in elevation of the terrain or in flight altitude as shown in Fig. 1 where the scale is

$$\frac{d}{D} = \frac{F}{H_0 - h}.$$

Relief Displacement.

Fig. 2 represents the relative position of the ground and a vertical photograph, the negative of which is parallel to the datum plane. A and its orthographic projection B, which have the same position on a true map,

* This was performed in co-operation with N.K.P.M (Standard-Vacuum), who also had their new concessions in Sumatra photographed from the air for the same purpose.

have different positions on the negative. The distance between a and b on the negative is called relief displacement, designated by e.

$$\frac{h}{H} = \frac{A'B}{A'N} = \frac{e}{r} \quad \text{or} \quad e = r \cdot \frac{h}{H}.$$

Thus, the relief displacements change proportionally with the distance from the centre of the photograph.

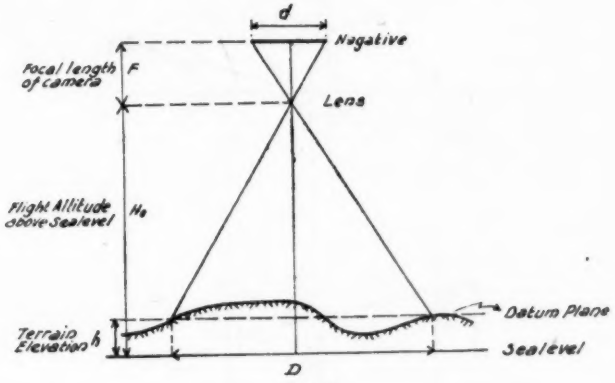

FIG. 1.

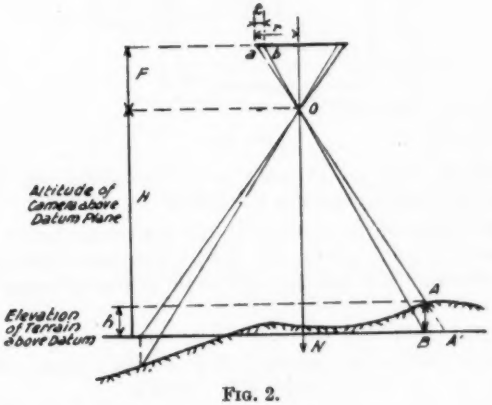

FIG. 2.

Distortion Caused by Tilt.

As can be seen in Fig. 3, tilt causes a reduction of the scale on the one side and an increase on the other side of a tilted photograph. In Fig. 3 the angle between the plumb-line and the optical axis of the camera is called the tilt angle ($i°$). To measure the distance of the plumb point from the principal point, the intersection of the collimation marks (see Fig. 7) on the photograph, we have to determine the length $CV = f \tan i°$. The

principal line is the intersection of the vertical plane through the optical axis and the plumb-line with the plane of the photograph. The intersection between the axis of tilt and the principal line is the isocentre (see also Fig. 4). Differences of scale, relief displacement, and distortion by tilt extend radially from the isocentre.

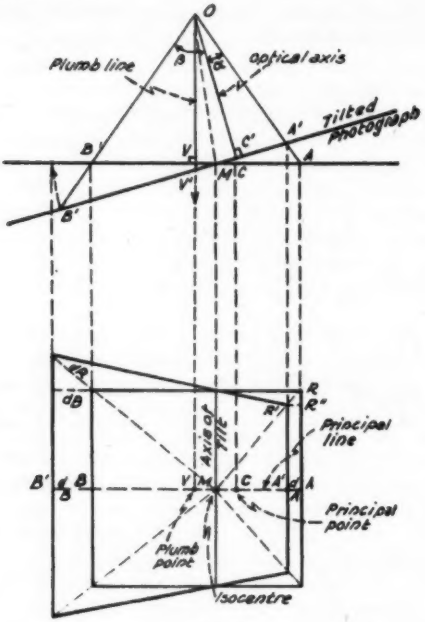

FIG. 3.

Angles Measured from the Isocentre in a Photograph are Equal to the Corresponding Horizontal Angles in the Terrain.

In Fig. 4 the plane of the photograph has been extended to the plane of the ground surface (intersection line XY). The same characteristic lines occur in Fig. 4 as in Fig. 3, but the angle of tilt is greatly exaggerated in the former.

$\angle\, C'M'O = 90° - \frac{1}{2}\, i°$

$\angle VMO = 90° - \frac{1}{2}\, i°$, hence $\triangle\, M'PM$ is an isosceles triangle, hence $PM = PM'$.

$\triangle\, PXM'$ is congruent $\triangle\, PXM$

$\triangle\, PYM'$ is congruent $\triangle\, PYM$

$\wedge\, M'_1 = \wedge\, M_1$

$\wedge\, M'_2 = \wedge\, M_2$

$\wedge\, M' = \wedge\, M$

The rule of the equality of angles in the terrain and in the photographs is of paramount importance in photogrammetry, the science of measurements

in photographs. For practical purposes the rule holds true for the isocentre as well as the principal point when one of the following conditions is fulfilled:

(*a*) when the terrain is almost flat;
(*b*) when the points have been corrected for relief displacement;
(*c*) when tilt of photographs is smaller than 2°.

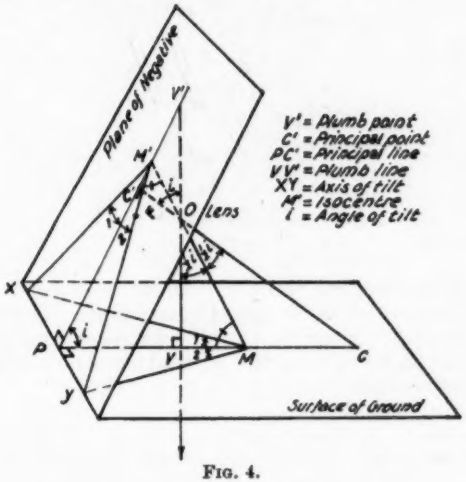

FIG. 4.

TWO-DIMENSIONAL RADIAL TRIANGULATION.

Radial triangulation is based on measurements of directions in the photograph from the principal point.

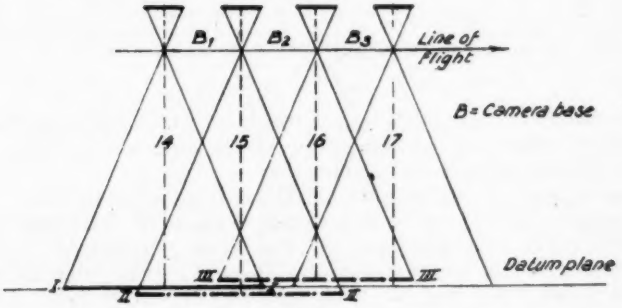

FIG. 5.

In aerial surveys photographs are usually flown in parallel flight strips and have an overlap of 60 per cent in the line of flight (Fig. 5) and 30 per cent in regard to the adjoining parallel strip.

As discussed above, due to variations in scale and to relief displacement, the images on the photographs do not appear at true positions. The directions measured from the principal point, however, are correct. In Fig. 6 the true position of a point p, appearing on photographs I and II as p_1 and p_2 respectively, can be found by intersection of two radial lines through the principal points of I and II.

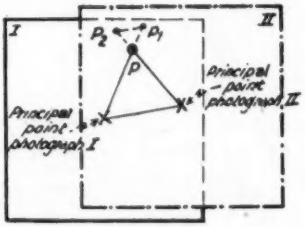

FIG. 6.

In Fig. 7 two points 15–2 and 15–3, called " pass-points " selected on photograph I appear also on the overlapping pictures II and III (see also Fig. 5). The same holds true for the principal point 15 of photograph II which has been transferred from one overlapping photograph to the other by means of a stereoscope.

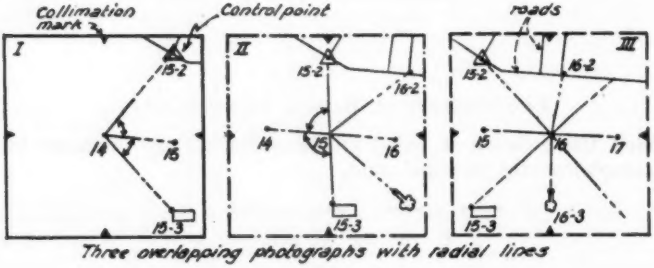

FIG. 7.

To obtain very accurately radial directions in the photographs, an instrument, called a radial triangulator, can be used which measures all angles with utmost precision in minutes.

Assuming a provisional azimuth and distance for the line 16–15, a " chain of triangles " (Fig. 8) can be constructed of which all the angles can be measured from the photographs. Provisional co-ordinates can be calculated for all the points contained in this row. If co-ordinates of two control points (15–2 and Mt Vernon in Fig. 8) are available, definite co-ordinates can be computed for all points.

Instead of computing the co-ordinates, a graphical triangulation can be carried out on transparent paper, beginning with a photograph showing points with known distance and azimuth, so that the correct scale can be determined. The chain of triangles can then be continued until other

control stations are reached. If the plot does not tie in to the control points an adjustment has to be made for all the points of the triangles proportional to the linear and directional error of the plot. Before the war grids comprising triangulation strips for large areas used to be made to which the so-called filling-in strips were tied in.

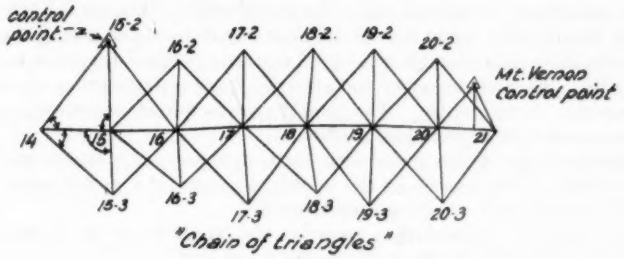

FIG. 8.

Slotted Template Method.

The method of graphical triangulation necessitates drafting afresh re-adjusted points on the final base map. To avoid this extra work transparent templates are used in the so-called "template method." The templates are cut to the same size as the photographs and the necessary directions from their principal points are marked on it. The templates can be moved in their corrected positions should any adjustment prove necessary.

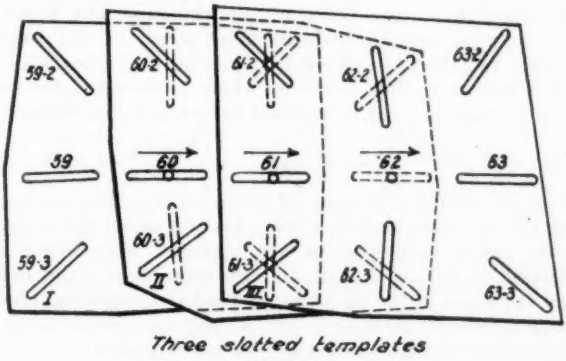

FIG. 9.

The "slotted template method," on the other hand, follows the same principle, except that radial rays from the principal points are substituted by radial slots punched in cardboard, Kodatrace, or thin aluminium plate (Fig. 9). Copper studs are inserted in the slots so that other templates may be joined thereto in such a way that free motion between adjoining templates is restricted to the directions of the slots which lie along the radial lines of each template. It will be remembered that radial lines are

peculiar to each photograph and therefore new templates have to be made for each photograph.

Metal Slotted Arm Method.

In this method metal slotted arms are made use of instead of templates. These arms consist of spring steel about 0·015 in thick and $\frac{1}{2}$ in wide, and have a round hole at one end and a slot at the other. The arms must be of varying length to fit radial rays of different length from the principal point. They provide a considerable saving of material because they can be used repeatedly. They are stronger and allow less play provided they are firmly held together in the centre. The geometric principle is, of course, exactly the same as for other template methods.

A disadvantage of this metal arm method, however, is that sometimes due to slight disturbances in the centring device the radial angles are likely to change with resulting serious errors.

More accurate triangulation requires the application of stereoscopy, some basic principles of which will be discussed later.

Rectification of Tilted Photographs.

The process of rectifying pictures for tilt entails the projection through the negative of the photographic image upon a screen or projection table on which the pass-points of the photograph have been marked. It will be remembered that the correct position of these pass-points can be plotted by radial lines for each point appearing on two overlapping photographs (Fig. 6). By projection of a tilted picture through its negative on the screen and changing the relative tilt of the negative, the lens, and the projection table, the points appearing on the projected image can be brought to coincide with the corresponding points on the screen. The rectified image can then be printed by replacing the screen with printing paper and a picture is thus produced which is corrected for tilt. This procedure is carried out in an instrument known as a "rectifier."

Mosaics.

In the case of controlled mosaics all pictures have already been rectified and scaled and are assembled on a base sheet on which the control-points acquired by radial triangulations are marked. Since distortions are smallest around the principal point, only the centre part of any one picture is used and the edges of the photographs bordering adjoining pictures are torn off rather than cut in order to give a good appearance to the mosaic.

In semi-controlled mosaics unrectified pictures are used.

Basic Principles of Stereoscopy and some of its Applications.

A single aerial photograph gives an image as a one-eyed person would see it. Binocular vision introduces depth perception and convergence. In one-eye vision convergence is lacking and the brain may report a large object to be far away or a small object nearby. The human optical system in fact is a short base range-finder with a base of $\pm$ 2·5 in, in which accommodation and convergence are linked up automatically.

Each eye forms a two-dimensional image of an object, but the image in the left eye is slightly different from that in the right eye, because both eyes see the object from a slightly different angle. These two different images are united in the brain to form a three-dimensional picture.

Obviously, the angle of convergence or parallax is the governing factor which determines the impression of distance. The nearer the object the greater the convergence of the optical axes of both eyes, the farther off the smaller the convergence.

In stereoscopy two photographs taken from two different points are observed separately by each of the eyes and again the two images are combined in the brain into one stereoscopic image.

In aerial photographs the parallax of a point is the change in the position of its image measured from the plumb point or principal point (P and P' in Fig. 10) on two over-lapping photographs.

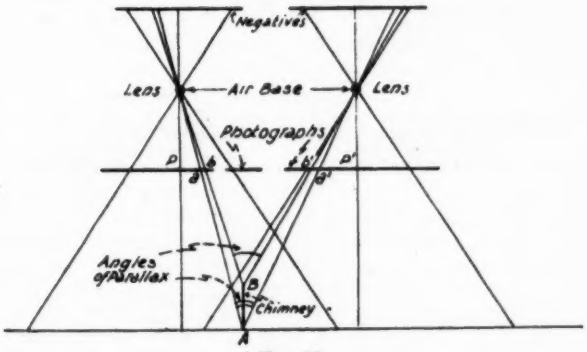

FIG. 10.

In a stereoscope the position of a point is observed by the left and right eye at different angles. The greater the angle the closer the image appears to the observer and illusion of space is thus created. In Fig. 10 the image points of A and B (base and top of a chimney) on the two photographs will be a and a', and b and b' respectively, a and a' being displaced a short distance from b and b'. By stereoscopic fusion a and a' as well as b and b' are combined to two single points representing A and B and the illusion is created that B is situated some distance above A.

In order to get a proper stereoscopic image of a pair of photographs they should be placed in such a way that the two principal points appearing on each photograph should all lie on a straight line, which actually means that they are orientated in the same way as the exposures during the flight.

Application of Stereoscopy in Photogrammetry.

An important means of determining differences in parallax and altitude in a stereoscopic image is the so-called "floating mark." Two thin pieces of glass, on each of which a point is marked, are connected by a rigged rod. This apparatus is placed on a pair of photographs. One glass is movable in

the direction of the axis of the rod by means of a micrometer head (Fig. 11), the other glass is fixed.

Each point is seen under the stereoscope at a different angle by each eye. Thus the image of the point appears to float in space. By shifting the one glass towards or away from the other, the floating point is seen moving vertically up and down in the stereoscopic image of the pair of photographs. The floating mark can be brought to coincide with any point on the stereoscopic image of the terrain. By readings on the micrometer head and the application of a simple formula, differences of altitude between any two points can be determined. This instrument is known under the name " stereometer " and is often used in photo-geology.

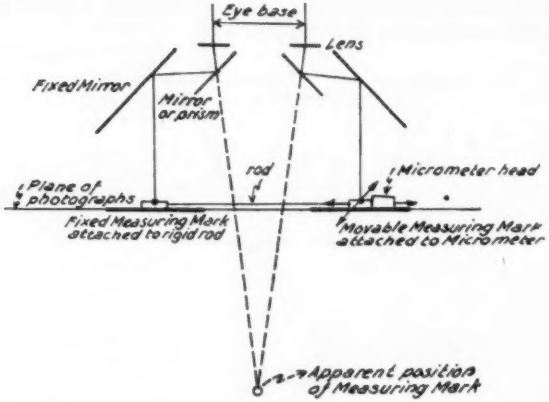

FIG. 11.

The stereoscopic principle has also been applied in instruments where the details of two adjoining pictures are projected so that corresponding rays intersect and where this is done either by actual optical projection or by materializing the rays by rods. In these instruments plotting is done with the help of two floating marks which are again visually brought in contact with the stereoscopic image. After two pictures have been orientated and measured, the first of the photographs is removed while the other is kept in position. A third adjoining picture then takes the place of the one removed and is measured in relation to the second one. The measuring is combined with an automatic plotting device. This method is applied in the so-called stereo-autograph or stereoplanigraph and is actually a three-dimensional triangulation.

In the stereomultiplex instrument up to twenty pictures are projected through reduced glass copies of the original row of photographs. Red and blue filters are used alternately in the projectors and corresponding rays are made to intersect by moving the projectors. Observed through spectacles with one blue and one red glass a stereoscopic image is obtained. Altitude as well as co-ordinates of any point in the stereoscopic image are directly measured by this method.

Types of Cameras and Photographs.

Most of the cameras used by the Shell group were of the single-lens type. Good and, in particular, economical results were obtained with a wide-angle single-lens camera of a focal distance of 4 in and covering angle of 74°.

Favourable results were also attained with the 8-in camera with covering angle of 65°, though before the war this camera was less economical than the wide angle one at the same altitude. However, since aeroplanes with a higher ceiling are now obtainable and crews are equipped with oxygen, the 8-in camera can be flown at a higher altitude and can operate under certain conditions as economically as the 4-in camera.

A camera equipped with nine lenses, known as " panorama camera," was successfully used in 1936 in Netherlands New Guinea. It consisted of one vertical and eight adjoining obliques projected by prisms on one film together with the octagonal, vertical picture. The negatives were transformed in a specially built transformer to eight vertical segments, mutually fitting around the central picture. These multi-lens pictures were compiled to form a navigational map for the detail flights with the 4-in camera.

In 1938 this panorama camera was also used for a rapid geological reconnaissance in Australian Papua.

Five-lens cameras were in use before the war. They are based on similar principles to the nine-lens camera.

In 1937 favourable results were achieved in North Borneo with a wide angle pendulum-camera. Alternatively one vertical and two obliques on each side of the flight line were taken. The exposures were timed in such a way that the verticals still overlapped by 60 per cent.

During the war cameras with extra long focal lengths (up to 100 in) were built. These were especially used for photo flights over enemy territory to make large-scale pictures from high altitudes (50,000 ft). As the coverage of these cameras is small they are uneconomical.

A further wartime development was the Tri-metrogon camera which became the standard outfit for the U.S.A.A.F. One vertical and two obliques are simultaneously taken from three cameras, each equipped with a 6-in lens with a cone of angular coverage of 74°. Both obliques overlap the vertical approximately 25 per cent. One exposure covers the flight line from horizon to horizon.

An interesting development is the so-called " continuous strip camera." A film, 9-in wide, or even wider, passes a slit aperture at a speed closely co-ordinated with the ground speed of the aeroplane. Thus a continuous strip of film up to 200 ft long is exposed.

Type and Scale of Photographs.

It is almost universally agreed that vertical photographs are preferable to obliques so far as photo-geological and topographical elaboration is concerned. This does not imply that obliques cannot be used to advantage for rapid reconnaissance. In fact they have been of great use in the past and, in particular, during the last war when vast areas had to be mapped in the minimum of time.

Before the war the Shell group had interpreted photo-geologically an

area of more than 200,000 square miles spread all over the world. The great majority of these pictures were verticals taken with single-lens cameras, among which the 4-in wide angle camera was most frequently used. Photographing was mostly done from an altitude of 4000 metres (12,000 ft) above the average height of the ground, the size of the pictures being 18 by 18 cm (7·2 by 7·2 in) and each exposure covered an area of 5200 hectares (21 square miles).

The 8-in camera flown at 6000 metres, giving pictures of 18 by 18 cm on a scale of 1 : 30,000, is preferable to the wide-angle camera in areas of pronounced topography since distortion away from the centre is smaller, the angle of coverage being smaller.

The nine-lens camera, known as the "panorama camera," with a focal length of 5·3 cm (2·1 in) makes vertical pictures of 24 by 24 cm (9·6 × 9·6 in). Flown at 4300 metres the scale of the pictures is 1 : 80,000, each picture covering 12,500 hectares (48 square miles).

Due to the distortion, these photographs are only suitable for photo-geological work if a rapid reconnaissance without detail is needed in an area of pronounced structural geology.

Quality of Photographs.

Pictures destined for photo-geological interpretation should have as little tilt as possible. Not only is the image of tilted pictures badly distorted, but even a slight deviation from the vertical of one of the photographs of a stereoscopic pair causes a strain on the eyes of the photo-geologist. Whilst the observer is capable of correcting parallax in the direction of the eye-base, focusing of deviations in a direction perpendicular to this base, as becomes necessary in tilted pictures, is harmful to the eyes.

In multi-lens pictures faulty transformation of the obliques into verticals quite often causes similar eyestrain.

It is of utmost importance that the photographic paper as well as the films used in the camera are free from irregular shrinkage, which in areas of flat topography can give rise to a "pseudo relief" in the stereoscopic image. This is easily detectable by the abnormal drainage pattern (see page 17). However, if rivers are lacking and the distortion remains consequently undetected such pseudo-relief can lead to an incorrect structural interpretation.

In the U.S.A. photo-geological interpretations were tried in areas with extremely flat-lying strata, dipping at not more than 50 to 100 ft per mile. It has been experienced in such areas that distortion caused by tilt or shrinkage made reliable structural interpretation impossible. Pictures rectified for tilt and printed from non-shrinkable film on non-shrinkable paper might yield better results. However, even if these conditions are fulfilled, only photo-geologists with exceptional stereoscopic ability might be able to detect structural data.

Principles of Photo-geology.

The geological data observed in the stereoscopic image of a pair of photographs are mainly deduced from the morphological aspect of the

landscape, from the appearance and characteristic forms of certain formations and from the nature of the vegetation.

Recognition of Structural Features.

The morphology or shape of the landscape is closely related to the composition and attitude of the strata at or near the surface. If layers of different hardness are folded or faulted and subjected to erosion the harder and more resistant beds survive longer than the softer ones.

The effect is that layers of various grades of hardness will show a different physiography. Hard layers are often eroded into asymmetric ridges, the one slope of which is steep and short, the other less steep and long. Both slopes are sometimes separated by a sharp linear ridge. The longer, more gentle slope forms a more or less regularly inclining plane, the inclination of which is representative of the dip of a particular layer. The two types of slopes are called in geological terminology the "scarpe" or "face slope" and the "dip slope." Dip slope and face slope show up remarkably well in the stereoscopic image of the terrain. In barren country these features are usually easily recognizable in the field, but in jungle-covered country with its obscure view they are mostly not visible on the ground.

The direction of dip of these dip slopes can be successfully estimated in the stereoscope. It can also be measured by means of the stereometer described above.

In terrain where the composition of the rocks is such that dip slope and face slope are not developed, small differences of hardness of layers sometimes show up as minor breaks in the slope all around individual hills. Again, under the stereoscope these breaks, even in open country, can better be detected than on the ground. In the stereoscopic image one actually observes the landscape as a giant, thousands of feet tall, and equipped with extremely sharp eyes, wide apart, would see it. His field of vision would be much larger than that of the observer on the ground who, even if he stands on a high point, obtains only a one-sided view of the greater part of the terrain.

If a break in the slope of a hill is marked on one of the photographs of a stereoscopic pair and thus accentuated, a photo-geologist trained in stereoscopic observation can estimate the direction of dip of the plane of the break. This dip is representative of a layer in the hill which is more resistant than the covering strata.

It will also be clear that sudden interruptions of characteristic beds and dip slopes as well as sudden changes in dip or topography, particularly if these occur along lines which can be followed over a considerable distance, might be suggestive of faulting.

The photo-geologist should also pay attention to the occurrence of terraces. These forms of landscape, generally horizontal, are found either along the coast or bordering rivers at various altitudes dependent upon successive changes in the level of the sea or river beds. Examples are known where these horizontal terraces are tilted or warped due to recent tectonical movements which may represent rejuvenated phases of folding of anticlines, more pronounced at depth. Recognition of such tilted terraces through the stereoscope can best be achieved by comparison of the plane of a meandering river bed which, over short distances, is nearly

horizontal with the plane of the terrace. A skilful interpreter is needed to recognize such tilts, and the phenomenon can only be detected in pictures free from tilt.

Different coloured strata are sometimes clearly visible in the photographs of open rocky countries and make it possible to see structural details even in single pictures or in mosaics.

Recognition of Geological Formations.

The form of the landscape, that is to say, the type of topography, may be characteristic of certain geological formations. For example, predominant round, smooth hills of one formation may contrast with sharp, long, narrow hills of another. In some territories entirely covered with dense jungle, typical giant rhomboidal joints show up which prove to be characteristic of limestone of a certain age. Limestones of different age appeared to have slightly different cleavage characteristics and could thus be distinguished.

The type of vegetation is often a clear indication of different formations, particularly in areas with widely scattered trees or areas covered with shrubs such as occur in semi-deserts and sub-tropical countries.

Differences of vegetation can also be indicative of different types of terrain in low-lying regions near the shores as is common in tropical countries. In New Guinea, for instance, it was possible to discriminate between salt-water and fresh-water swamps and to distinguish dry, flat land (terraces).

Checking of Photo-geological Interpretations.

It must be emphasized that a geologist engaged in interpreting photographs should pay regular visits to the terrain in order to check his structural and formational interpretation on the spot. If this is not carried out at an early stage he runs the risk that errors are repeated over a wide area and that at a later stage the interpretation might have to be revised with consequent waste of much valuable time.

Short reconnaissance flights over the area at medium altitude might also prove useful in this connexion.

Methods of Elaboration of Photographs.

All the observations on each picture should be systematically marked on compilation maps.

A satisfactory system adopted by the Shell group makes use of so-called groups tracings, consisting of strips of non-shrinkable Kodatrace paper of a size covering six to eight overlapping pictures. Part of the transparent strip is made to cover the left photograph of a pair, the remaining part underlying the one on the right. The principal points of both overlapping pictures, which should be marked on the photographs in advance, are copied on the groups tracing. The four principal points (two on each picture) are orientated on one line and the distance between the two photographs is adjusted in accordance with the principal distance of the stereoscope. If the stereoscope is equipped with magnifying glasses which of course cover only a portion of the photographs, the instrument, in order to guarantee a proper stereoscopic image at any point on the two pictures,

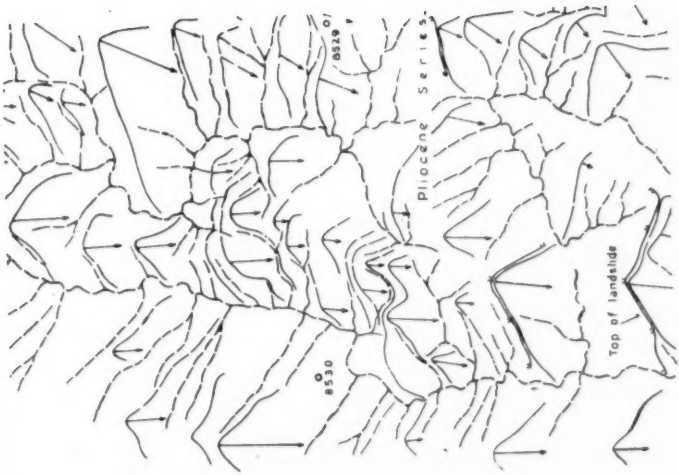

PLATE 1.

PLIOCENE SERIES, CONSISTING OF SANDSTONES, CLAY-SHALES AND CONGLOMERATES WITH EXCELLENT DIPSLOPES. DEEPLY INCISED V-SHAPED VALLEYS AND SHARP TRIANGULAR RIDGES ARE CHARACTERISTIC.

[*To face p.* 530.

PLATE 2.

PLIO-PLEISTOCENE SERIES REPRESENTED BY SHALES, SANDSTONES, AND CONGLOMERATES, GENTLY FOLDED. DIPSLOPES ARE NOT SO WELL PRONOUNCED AND LACK THE SHINGLED SUCCESSION OF PLATE 1.

PLATE 3.

TWO ANTICLINES (I AND II) IN "PINNACLE" LIMESTONE OF MIOCENE AGE. SEVERAL VERY LONG, DEEPLY INCISED JOINTS AND SINK-HOLES.

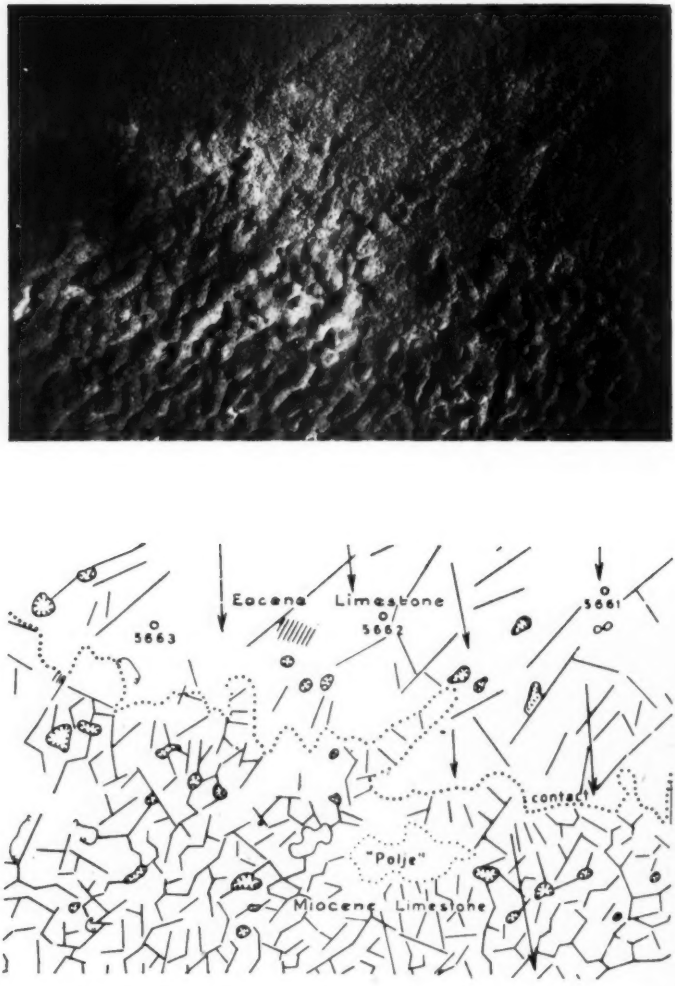

PLATE 4.

CONTACT BETWEEN MASSIVE LIMESTONE OF EOCENE AGE AND MIOCENE LIMESTONE WITH WELL-DEVELOPED "PINNACLE" STRUCTURE AS WELL AS CIRCULAR AND ELLIPTICAL DOLINES.

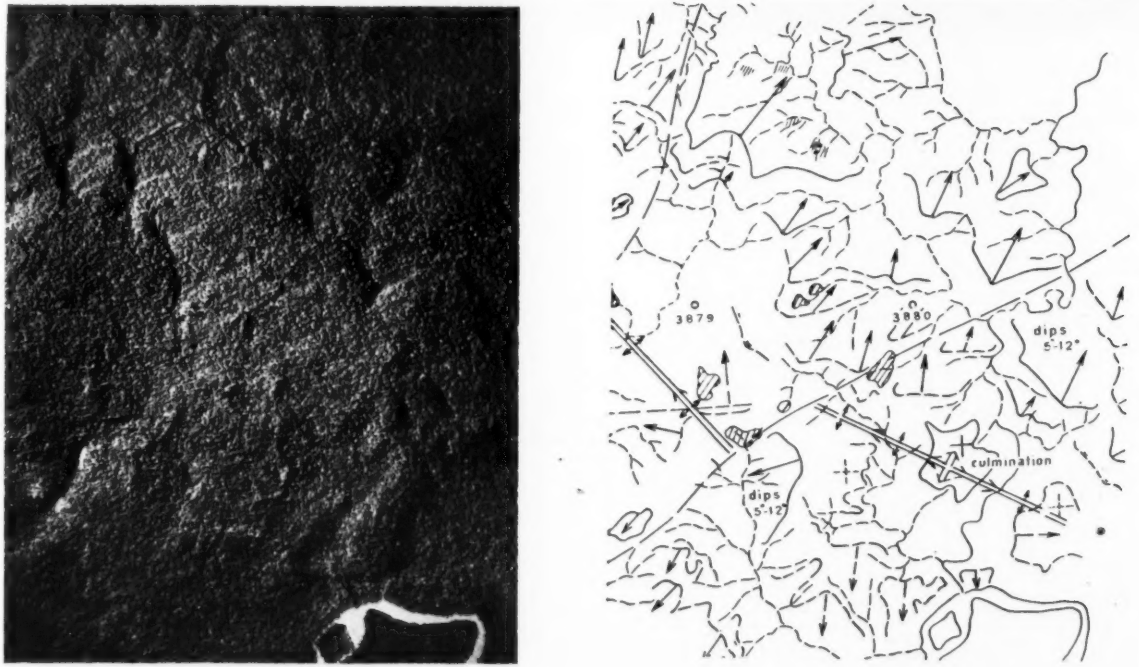

PLATE 5.

DIPSLOPES SHOWING A CULMINATION WITH FLAT APEX. NOTE SHARPLY VISIBLE OUTCROPPING HARD BEDS AND LESS DISTINCT ONES MARKED WITH DOTTED LINES. AXIS OF ANTICLINE OFFSET BY FAULT.

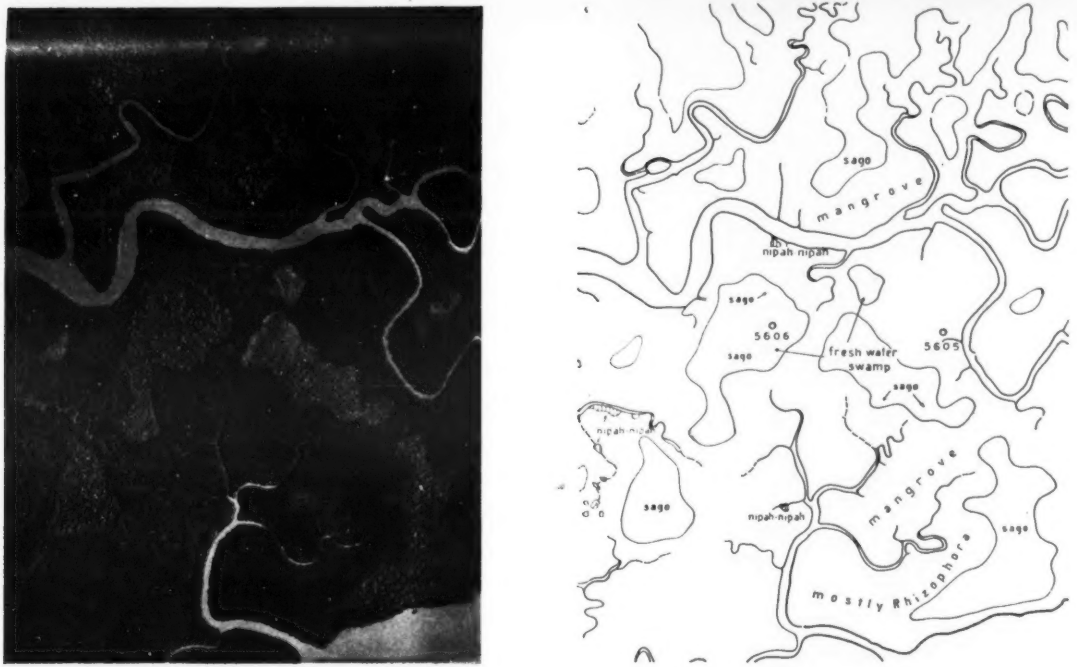

PLATE 6.

DIFFERENCES OF VEGETATION IN SWAMPS. LIGHT SPOTS INDICATE FRESH WATER VEGETATION; SURROUNDING BRACKISH WATER VEGETATION HAS DARKER APPEARANCE AND CONSISTS OF "MANGROVE" WITH MUCH RHIZOPORA.

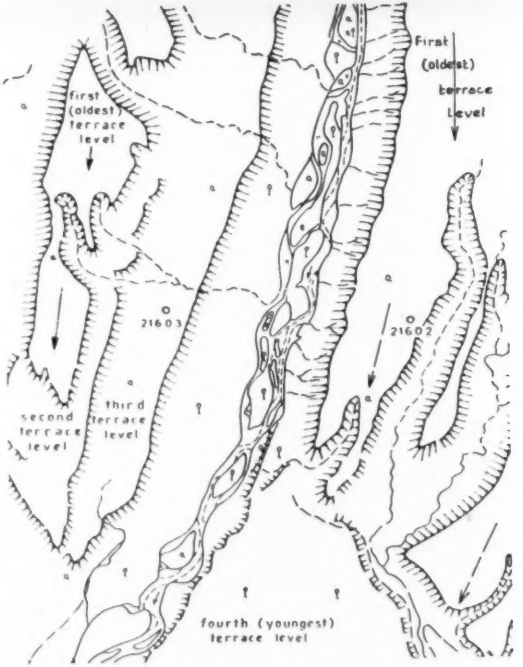

PLATE 7.

FOUR TERRACE LEVELS, SLIGHTLY TILTED. NOTE POORER VEGETATION ON TOP OF THE HIGHER TERRACES.

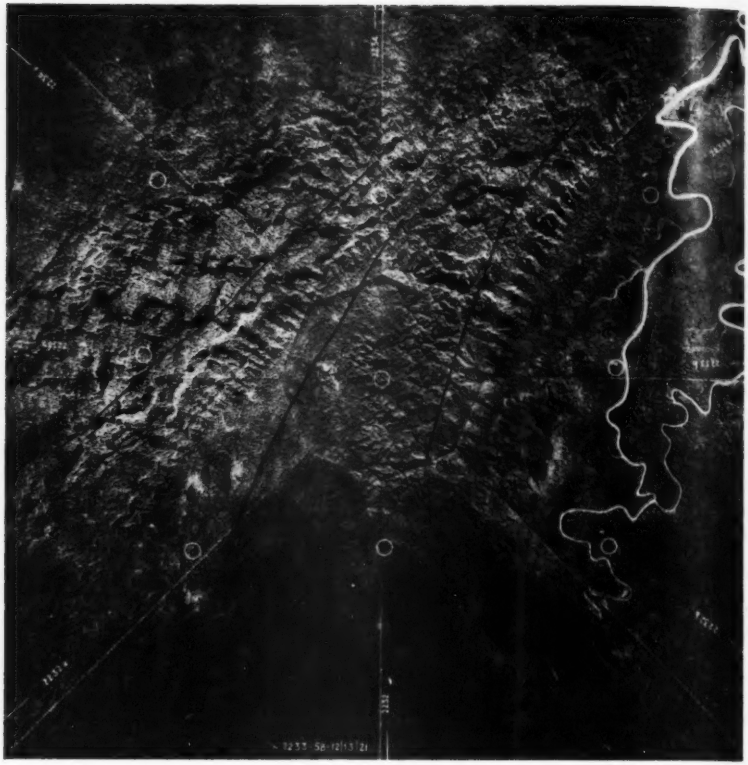

Plate 8.

NINE-LENS PHOTOGRAPH AFTER TRANSFORMATION TO ONE VERTICAL PICTURE. STEREOSCOPIC IMAGE SHOWS MARKED DISTORTION AWAY FROM CENTRAL POINT PARTICULARLY IN HILLY PART. STRUCTURAL STEREOSCOPIC INTERPRETATION REVEALS TWO ANTICLINES SEPARATED BY SYNCLINE.

should be moved parallel to this principal line when another part of the photographs has to be examined. In order to achieve this, the stereoscope is mounted on a so-called parallel guide.

All the geological observations are marked on the groups tracing according to a specially prepared uniform system of symbols. For reasons which are explained below topographical features, such as river systems, divides, differences in vegetation, open clearings in the jungle, villages, roads, and any other non-geological observation of particular interest are also indicated on the tracing.

After the left photograph has been fully interpreted the groups tracing and the left picture (No. 1) are removed, photograph No. 2 put in its place, and No. 3 substituted for No. 2. The groups tracing is then reinstalled so that the principal point of No. 2 which had been indicated on the tracing during interpretation of No. 1 covers the principal point appearing on picture No. 2. Interpretation of No. 2 proceeds in the same way as that of No. 1, and so on, until No. 8 is reached. A new groups tracing is then introduced and the interpretation of pictures 9 to 16 carried out.

The various groups tracings are tied into a base map with control points which have either been calculated, or derived from graphically triangulated runs of photographs, or from triangulation runs worked out according to the slotted template method.

Due to tilt and inaccuracy of scale of the individual pictures there usually exists a difference of distance and azimuth between control points on the base map and corresponding points on the groups tracings. These differences are adjusted by photographic reduction or enlargement of the groups tracings in a photostat.

Advantages of Studying and Marking Topographical Features.

The advantages of marking topographical features are manifold.

The indication of the river system, including the tributaries and divides, enables the explorer to get a general impression of the topography of the terrain and its best way of approach.

Study of the drainage pattern sometimes yields also valuable geological information.

For example, in terrain built up of gently dipping beds and low hills without any marked features, such as dip slopes and breaks in slope, an asymmetric drainage pattern may have geological significance. In such a pattern the divide bordering a valley may run on one side of the river for a considerable distance nearer to the river bed than the divide on the other side of the river. This might be an indication that the strata dip gently from the distant divide towards the valley.

Sometimes abnormalities in the river system may be indicative of recent tectonical movements. For example, in some countries where the main rivers transport an abundance of sediments from higher regions to the low lands during the rainy season, inundations cause deposition of a certain amount of sediments on both sides of the river bed. These so-called "distributary ridges" form a narrow belt of young deposits of, say, 1 or 2 miles wide and 5 to 10 ft high all along the stream. The slope of these ridges towards the sea, of course, is in accordance with the fall of the river. On aerial photographs of coastal plains relics of distributary ridges are

sometimes discovered, indicating that the original river bed has changed its course. Sometimes these very gentle old ridges, which in general also slope gradually towards the sea, are locally crossed by small, recent river beds and it appears that between two depressions the distributary ridge is slightly uplifted. Topographical expressions of this nature might be indicative of young tectonical movements either caused by rejuvenation of deeper folds or, in some instances, by young domal movements above rejuvenated salt domes. It is obvious that in cases like this important indications of geological conditions in the underground might be discovered which can be of particular interest to the explorer for oil.

Also alignments of successive bends in different rivers and sudden deviations abnormal to the general drainage pattern may be indicative of fault lines.

Drawing of the drainage pattern may further benefit the interpreter when examining an area of flat-lying strata where pseudo-stereoscopic effect appears owing to defect in the prints (see page 13). Depressions or slight doming can easily be recognized as spurious by the impossibility of the drainage pattern.

Roads, villages, and clearings in the jungle are of particular interest to the explorer in connexion with his plans for visiting the country and are, moreover, of help for orientation once he has entered the jungle.

In heavily wooded virgin country the geologist often follows the beds of small creeks where exposures of rocks are usually more numerous than in larger streams. He may lose much of his valuable time when he does not have a photo-map and the river bed appears to run in the wrong direction. Careful observation and marking of small valleys, which are often not visible to the naked eye, but are distinguishable through the stereoscope is therefore of utmost importance.

Applications and Specifications of Geological and Topographic Air Maps.

Geological Maps.

If all the observed data are systematically assembled the oil geologist disposes of a wealth of geological information regarding the territory on the greater part of which he has never set foot.

The properly located dips and boundaries of beds and occurrences of different formations enable the geologist to work out a structural map which can be of great help in selecting areas where structural conditions for accumulation of oil are favourable and which ought to be earmarked for investigations in detail on the ground. Some areas might be discarded because of adverse structural conditions while others where structural indications are lacking might be selected for geophysical investigations.

Convenient scales for geological compilation maps proved to be 1 : 250,000, 1 : 100,000, and 1 : 25,000. Maps based on a graphical triangulation were found to be fully satisfactory for reconnaissance purposes.

The method of compiling geological line maps from groups tracings obviously requires much drafting and involves a considerable amount of time. Some people prefer a quicker method whereby the photo-geological data are directly plotted in black ink on the pictures. Thereafter an

uncontrolled mosaic is assembled and a photographic negative made and printed on the scale required.

This method has been applied in countries where colour differences in beds, as well as structural features, showed up very clearly due to lack or scarcity of vegetation and due to the geological nature of the terrain.

The application of uncontrolled mosaics, however, must lead to inaccuracies. Moreover, this method can hardly be applied in areas where interpretation is difficult and where the examiner has often to change his original conception after the study of other photographs in the same run or in side-runs. Furthermore, differences of vegetation and many other features of importance are not brought out separately in this method and are apt to be overlooked by the field geologist who deals only with the mosaic interpretation.

Although it is widely recognized that the mosaic method can be applied to great advantage in open country where conditions of interpretation are exceptionally favourable, for regions with a thick cover of tropical vegetation the groups tracing method, in our opinion, is preferable.

Topographical Maps.

If concessions have to be staked or where property boundaries have to be surveyed it may become necessary to have a much more solid geodetic base than the graphical triangulation.

In some countries the Government requires certain specifications to be fulfilled. In this case the slotted template method may be successful or a three-dimensional triangulation with the multiplex, stereo-autograph, or stereoplanigraph might be necessary.

It always pays to have the actual photography done as accurately as possible and to adhere particularly to the strict requirements regarding tilt, overlap, and quality of films and prints. If the photographs are correctly taken, glass diapositives can be made which can easily be stored without the danger of shrinkage. If necessary, accurate contour maps can then be made of any area at any time either with the multiplex or stereo-autograph. For instance, in this way excellent results have been obtained in connexion with road building in jungle country where the actual photoflights took place more than ten years ago.

The slotted template method has been used to great advantage for the compilation of property maps in the U.S.A., where, as is known, these maps are indispensable to oil companies in connexion with their leasing activities.

Possible New Developments and Applications.

Colour Photography.

In open country with light vegetation, formations sometimes show marked differences in colour which are not distinguishable on black and white photographs.

Already before the war, attempts had been made to bring out these differences photographically from the air. Experiments to achieve this by making use of special filters and exposure-times did not meet with success. The differences in colour usually proved not sufficiently contrasting to cause differences of shades in the pictures.

Experiments were also made with a so-called telechrome-camera with two lenses yielding two pictures on one glass plate. One of these pictures is taken through a red and the other through a green filter. These pictures are examined in a special apparatus in which the portion of the photograph taken through the red filter is illuminated through a red screen while that taken through the green filter is illuminated through a green screen. Both pictures are united into one by the optical system of the apparatus. Blue light is also projected on the combined red-green picture. It was found that only very bright colours could be satisfactorily reproduced by these instruments. Although areas were chosen where differences of colour were distinct on the ground the photographs taken from altitudes varying between 17,000 and 6000 ft did not yield encouraging results.

Experiments have further been made with ordinary colour-photography on Kodachrome films. One of the disadvantages is that these films require long exposures, causing blurring when used in air photography. During the war, colour emulsions have been developed that were more rapid and yielded better results. No satisfactory method of making coloured reproductions has, however, yet been found. Moreover, the effect of the atmosphere on colour differences has proved to be most disturbing. Summarizing, it can be said that colour photography in air mapping is still in an experimental stage.

Use of Special Emulsions.

Experiments were made before the war with panchromatic supersensitive infra-red aerofilm. The infra-red pictures were compared with ordinary ones made on supersensitive panchromatic films.

In heavily wooded areas a marked difference appears in infra-red pictures between needle-leaved and deciduous trees. The foliage of the latter, moreover, shows a somewhat greater variety of shades. The woods also appear less dark, which causes some improvement in stereoscopic effect. Another difference with ordinary pictures is that, in general, damp places appear darker in infra-red photographs, which sometimes causes a small drainage pattern to show up better in open country. The superior haze-cutting quality of infra-red film was once more confirmed.

These advantages, however, were outweighed by the fact that the infra-red films, as a rule, showed less detail than the high contrast panchromatic super-sensitive ones and that no important geological features could be traced which did not also appear on ordinary pictures.

Improvement in infra-red emulsions and filters might still achieve results superior to those obtained before the war so that new experiments might yield better results.

Emulsions of very fine grain may stimulate the use of enlarged photographs and thus bring out details which are not recognizable in coarser grain films.

Application of New Type Cameras.

A useful application of the continuous strip camera is the location of the line of flight of an aerial magnetometer. A small size strip of film (1·4 in wide) is continuously exposed and time-points are registered on this film simultaneously with the marking of time-points on the magnetometer curve.

Designs for using two strip cameras in order to obtain pairs of strip photographs which can be observed under the stereoscope are still in the experimental stage.

The Tri-metrogon camera was used during the exploration of the U.S.A. Naval Petroleum Reserve in northernmost Alaska, where flight strips 20 miles apart were flown at 20,000 feet. The photographs were also made in connexion with an airborne magnetometer survey. A preliminary geological interpretation was made for general reconnaissance purposes.

In conclusion it can be stated that the continuous strip camera represents the only striking new development in aerial photography during the last war. All the other methods used had mostly already been applied by oil companies prior to 1939. Even the Tri-metrogon camera is an improved and simplified version of a five-lens camera producing one vertical and four obliques which was already generally known in 1936.

Possibly the application of radar in air mapping as a means of accurately locating the position of an aeroplane at each moment an exposure is taken, and a new system of stabilization of the camera, might introduce revolutionary changes in plotting from aerial photographs. As far as we know, the solving of the problem of the application of radar is already in an advanced stage in the United Kingdom.

Acknowledgement.

The author is indebted to the management of the Bataafsche Petroleum Maatschappij for permission to publish this paper.

Discussion.

The Chairman (Mr T. Dewhurst): I am sure you will agree that Dr Taverne has presented his valuable paper in a most attractive way. I find it somewhat comforting to learn that the photographers cannot dispense with the services of the geologists; indeed, I predict that the geologists' services will be necessary until the camera is able to collect fossils and other specimens!

There are present this evening members who are experts in photo-geology and who are well qualified to discuss the technical aspects of the paper. We wish to make the most of the time available for discussion, and I do not propose to comment further on the paper.

Dr W. L. F. Nuttall: At different times I have had occasion to compare photo-geological maps with the maps of the geologists in the field. It is very interesting to make those comparisons because what comes out clearly is that the quality of photo-geology interpretation varies very greatly with the individual. Some men can interpret photographs three-dimensionally much better than others.

It is important that a photo-geologist should have a very sound geological knowledge; in addition, as far as possible, in the course of the survey or immediately after the survey, opportunities should be given to him or to men associated with him to go into the field and check some of his interpretations in order to ensure that he is working on the right lines.

A further point, which perhaps has not been sufficiently emphasized, is

the enormous saving of time that is effected by photo-geological survey. You may have to deal with an area, such as New Guinea, where no geologist has been. As a result of aerial survey it is possible to delineate the areas of interest and to eliminate a large part of the country from survey on the ground. It is not necessary to go to the expense in time and money of sending geologists to do a lot of work to find out where the promising structures are and where the subsequent work should be concentrated. Furthermore, even in an area where a fairly good geological map is available, photo-geology can bring out elements of structure which were not known previously or were not fully understood. Faults and unconformities have frequently been mapped much more accurately by photo-geology than by investigations on the ground, particularly in jungle country.

Reference has been made to the exactitude with which tectonic features and geological formations can be determined from photographs of desert country. After the accuracy of the initial photo-geological interpretation has been confirmed the photo-geologist can then sometimes go ahead and prepare a geological map showing the stratigraphical subdivision.

I understand that during the war the United States Army Air Force, employing a trimetrogon camera, took a large number of photographs in different parts of the world. Perhaps the lecturer can tell us to what extent has it been possible to use the obliques for the photo-geological interpretation work.

MR P. EVANS: My experience has been that a photo-geological map is of very great value whether the geologist has been to the area or has still to examine it. Even if an ordinary geological map is available, additional evidence will almost always be obtainable from the photographs. I should like to ask Dr Taverne what he thinks is the best relation between the field-work and the interpretation of the photographs. A possible arrangement is for the geologist to spend a short time in the field on reconnaissance, then to return to headquarters, to work out the photographs, and finally to go back to the field to get what additional information is necessary. There are several alternatives. For example, there may be a preliminary rough examination of the photographs followed by field-work and after that the detailed study of the photographs.

I think there are considerable advantages in having every field geologist trained in stereoscopic examination of photographs, so that he can himself make use of photo-geological methods.

There are different views about organization of photo-geological work: it may be centralized at headquarters under a specialist, or distributed so that each field geologist does his own interpretation. It would be interesting to have Dr Taverne's opinion of the relative merits of the two arrangements.

COLONEL J. S. SHEPPARD (Mining Department, Imperial Institute): It is most appropriate that the Institute of Petroleum should have secured a paper on air survey, bearing in mind the considerable amount of work that has been done by the oil companies and the development that has been made or is contemplated by the oil companies. I was rather disappointed when I had read the paper, because I felt the author had not given us sufficient specific examples of the general principles he has laid down. He

has stated that he is dealing with principles, and he has certainly covered them very well; but I would have welcomed a number of specific, concrete examples of the various principles he has given us. However, he has since met that criticism to some extent by his illustrations.

Dr Taverne will agree with me, I think, that most of his paper—at any rate, the second part—results from practical experience; and no one is more fitted to give us the results of his practice than is Dr Taverne. But he did disappoint me in not giving more examples, particularly with regard to the photo-geology of formations that he has found, where they were, and exactly what rocks were seen in the photographs.

Reviewing the second part of the paper, I cannot quite agree that the trimetrogon camera was standard in the U.S.A.A.F., although it is one that they used; only the 1/500,000 air maps and other maps of very small scale were made from trimetrogon photography.

I agree that oblique photographs are not of so much value as verticals. The Canadians, who first developed the use of oblique photographs, have abandoned it entirely, except for surveys for 1/500,000 air maps.

With regard to the principles of photo-geology, I would like to stress the importance of training, as an earlier speaker has done. One would not ask a skilled photo-interpreter to interpret a photograph for geology, nor is it right to expect a skilled geologist to be able to interpret geology from air photographs. This work does require training; but that is not appreciated by many responsible geologists, including even some of my academic colleagues, who look at photographs for the first time and say that they cannot learn much from them. Both training and practice are required, including visits to the ground in order to implement what one has learned from the photographs.

Coming to the section of the paper dealing with new developments and applications, I have seen some excellent vertical colour photographs taken, I think, by the Aero-Services Corporation of Philadelphia, using glass plates. They have some excellent photographs, including some low obliques, using a focal-plane shutter with differential speeds.

Finally, with regard to the possible application of Radar in air mapping, I would draw attention to a paper recently published by Professor Hart on "Surveying from Air Photographs Fixed by Remote Radar Control." It was first presented at the Empire Scientific Conference in 1946, and has since been republished in "The Empire Survey Review, 1947." It gives photographs and explanations of experiments made during the war, together with the results achieved.

I congratulate Dr Taverne on his paper. I know how much hard work goes into the preparation of a paper, and I think the Institute could with advantage secure further papers on aerial photography.

Mr. N. L. Falcon: My qualification for speaking is that I happen to have mapped in the field and on the ground in Persia about 20,000 square miles, and to have devoted a good deal of time to photographs.

Mr. Evans has asked whether we should have a centralized department in which people are dealing only with photographs, or whether the field-worker should also work on the photographs. I am absolutely convinced that the thing to do is to mix office-work and field-work as much as possible.

There must, of course, be a central office in which most of the photographic work is done, but I personally would like to see every field-man pass through it and become experienced in handling photographs, finding out how much can be done and how much cannot be done.

As an example of a piece of country in which photographs can be extremely helpful the coastal Makran area is ideal. I spent more than a year in that extremely unpleasant country. We had no base maps at all. That work was done before aerial survey became the custom. I was under the impression at the time, and I have still the impression that, if we had had small-scale photographs, the whole of that area of 10,000 square miles of country could have been geologically surveyed on the ground in a comparatively short time; and instead of spending 75 per cent of our time getting out a topographical background on which to record our observations, that could have been done for us by photographs beforehand.

MR. T. D. WEATHERHEAD: A point which I think is very important and which the author probably had not time to dwell upon is the necessity for the closest co-operation between the photo-geologist and the operators who are responsible for taking the photographs and for producing maps afterwards. That co-operation is absolutely vital.

The planning of an air survey is a very complicated operation, since it is essential to know first of all what types and degree of information is required from the photographs which are to be taken. It is by no means the case that any type of photograph will produce any type of information. Consequently, it is also essential to have the closest co-operation between the people concerned with the planning, and those for whom the survey is to be made, to determine the right scale of photography, the type of camera to use, and the type of filter to use.

To give an example; my company photographed many thousands of square miles in the Middle East last year over different types of terrain, and undoubtedly in many of those areas better results could have been produced if we had been supplied with detailed information of the type of rock, etc., which had to be photographed, and of the results that were required afterwards. We should then have known the best way in which to produce those results.

Oblique air photographs are of considerable use, I understand, to geologists; we have undertaken considerable oblique photography as an addition to vertical photography. We understand from the chief geologists in the field, employed by the companies for which we were operating, that those obliques have been of considerable use.

Recently I have seen photo-geologists of the Anglo-Egyptian Oilfields Ltd. in Cairo, who showed me excellent mapping from aerial photographs. Certain vertical photographs puzzled the photo-geologist completely and had puzzled them until they had come across the obliques which made the type of structure apparent.

DR TAVERNE, replying to the discussion, said: I am in full agreement with Dr Nuttall's views on the desirability of checking his photo-geological interpretation in the field. Actually this practice has been followed wherever it was feasible. I am of opinion that this type of field-trip should be made at an early stage in the photo-work so that the geologist can

correct any errors made, can improve on his interpretation, and can avoid faulty interpretations being repeated. Besides geological deductions, conclusions regarding the condition of the terrain are of considerable importance. For instance, in flat areas, certain types of vegetation are characteristic for marsh land, other types for dry land. Discrimination between these two types of terrain is particularly interesting to the geophysicist for outlining his geophysical survey. Therefore a check up of the conditions of the terrain is very desirable.

All this has also a bearing on the question of organization of photo-geological work raised by Mr. Evans. I am all in favour of combining photo-geological work and field-work. It is true that some oil companies have been doing a substantial amount of photo-interpretation in central departments. The reason for this was generally that a field organization for working-out the photographs on the spot was lacking and/or that trained photo-geologists with field experience were not available near the terrain. Personally I consider it definitely better that the photo-geological work should be done as close to the field operations as possible and that the photo-interpreter should visit the field from time to time.

Reference was made by Dr Nuttall and Col. Sheppard to the trimetrogon camera and to the use of obliques in general for photo-interpretation. During the war this camera was used on a very large scale in the Far East by the U.S.A.A.F. and recently it has also been used to advantage in the so-called U.S. Naval Reserve No. 4. in Alaska. Although the trimetrogon camera has rendered good services for a quick reconnaissance of large areas, it is generally agreed that it is not particularly suitable for detailed photo-geological studies. This does not mean that obliques in general cannot be profitably applied for amplifying geological interpretations derived from vertical photographs. In fact, I share Mr Weatherhead's opinion that there are cases where the study of obliques—including stereoscopic studies of overlapping obliques—has yielded valuable results.

Dr Nuttall further drew attention to the fact that the quality of photo-interpretation varies greatly with each individual interpreter. I should like to state that apart from the geological and physiographical experience of the photo-geologist an important part is also played by his stereoscopic ability. In areas with clearly marked topography and pronounced tectonical features the structural-stratigraphic interpretation does not present any unsurmountable difficulties to the photo-geologist of average capacity. However, if structural conditions show up less distinctly, as for instance in slightly rolling or almost flat areas with layers dipping at very low angles, the geologist faces a different problem. He should then not only possess an outstanding stereoscopic ability, but also be fully experienced in interpreting the physiographic characteristics of the terrain, to arrive at a reliable conclusion regarding tectonical conditions. In this case the photographs should be of high quality, that is to say tilt should be eliminated as well as any distortion of the stereoscopic image caused by irregular shrinkage of printing paper or film.

Mr Weatherhead is quite right in pointing out the necessity of close co-operation between the photographers and geologists. Both experts should consult each other frequently in order to achieve the best results from the most suitable photographs.

With regard to colour photography I share Col. Sheppard's opinion that some excellent vertical colour photographs have been taken. Experiments with colour photography have also been made with continuous-strip cameras and have met with some success. By using two such camera's and projecting the coloured images from each camera through differently polarized filters, a stereoscopic image was seen by observers wearing differently polarized glasses. However, these pictures were taken from low altitude under ideal weather conditions. Even a slight haze which, in black-and-white photography, can easily be cut out by the use of filters, seems to hamper considerably any colour photography. Moreover, making coloured prints for study under the stereoscope is a costly and slow procedure. All in all it seems that various difficulties will have to be surmountel before colour photography can be economically and successfully applied in photo-geology.

As to the application of Radar in aerial photography I understand that in Tanganyika and Nairobi experiments of this nature are under way. I am not familiar with the details of Professor Hart's paper but have been informed that the flying was done there in wide, concentric circles.

COL. SHEPPARD : The article refers in detail to work already done; but they are doing further work in that country.

DR TAVERNE : I understand that flying in wide circles is the best method for determining the exact location of the aeroplane during the photo-flights. Fixation of the exact position of the camera at the time each photograph is taken would, in my opinion, be of paramount importance and could lead to considerable economies in aerial surveying.

I now come to the remarks made by Col. Sheppard regarding the emphasis laid in my paper on a number of photogrammetric principles. I did so on purpose. My experience is that geologists who indulge in photo-geological work often do not pay enough attention to the photogrammetric basic principles which should be fully familiar to them. If they do not recognize the inaccuracies and limitations of aerial photographs—single pictures as well as mosaics—they might arrive at a wrong interpretation. This is particularly true in the case of the territories with low-dipping strata and ill-defined topography referred to earlier. Col. Sheppard also suggested that I should have enlivened my paper with more practical examples and amplified it with illustrations of the photo-geology of formations. I agree that there is room for enlargement. However, I am afraid that in order to meet Col. Sheppards requirements it would almost have been necessary to have written a book on the subject. Unfortunately lack of time prevents me from undertaking such a task.

VOTE OF THANKS.

THE CHAIRMAN : I am sure it is your wish that I should on your behalf thank Dr Taverne for a very valuable paper, and for the great amount of work which its preparation and presentation has entailed. I am sure you will wish to signify your appreciation in the usual way.

(The vote of thanks was accorded with enthusiasm, and the meeting closed.)

THE INSTITUTE OF PETROLEUM.

An ordinary General Meeting of the Institute of Petroleum was held at Manson House, 26, Portland Place, London, W.1, on Wednesday, April 14, 1948, Mr E. A. Evans, M.I.Mech.E., F.R.I.C., (President-Designate) in the Chair.

The Minutes of the preceding Ordinary General Meeting of the Institute, held on March 10, 1948, were read, confirmed, and signed.

Mr George Sell (Publications Secretary) read the list of elections to the membership of the Institute, and the Chairman commented that the length of that list indicated the very healthy condition of the Institute.

The Publications Secretary announced that the Annual General Meeting of the Institute would be held on Friday, April 30, 1948, in the lecture hall of the Royal Society of Arts, John Adam Street, Adelpi, London, W.C.2, and gave notice of resolutions to be submitted on that occasion *re* alteration of certain existing By-Laws. Following that meeting, the Presidential Address would be delivered by Sir Andrew Agnew.

The Chairman: I should like to emphasize the importance of the Annual General Meeting on April 30. Some of you may feel that an Annual General Meeting is rather a tiresome sort of show and that it is not worth while going. That is not the case at all, and I do ask you very earnestly to attend. The affairs of our organization are tremendously important; and if our By-Laws are not carefully considered we may be doing the wrong thing. We do ask you for your advice and your support at that meeting.

We have with us Mr S. T. Minchin, who will present his paper on "An Account of Some Solid State Properties of Petroleum Waxes in Terms of their Composition." I feel sure that those who have read his very long paper will agree that he has given this subject a great deal of thought. As a Research Chemist of the Burmah Oil Co. Ltd., he is very well qualified to deal with it.

Mr Minchin then presented the following paper:

AN ACCOUNT OF SOME SOLID STATE PROPERTIES OF PETROLEUM WAXES IN TERMS OF THEIR COMPOSITION.

By S. T. MINCHIN (Fellow).

THE COMPOSITION OF PETROLEUM WAXES.

PUBLISHED work on petroleum waxes may be said to provide very strong evidence that their main component is a portion of the range of the *n*-paraffin series that is solid at ordinary temperatures, but that other solid or semi-solid hydrocarbons are also often present, usually in substantially smaller quantities.[1-6] These latter are considered to be branched and cyclic paraffins.

Such deductions arise nearly always from an interpretation of various physical tests. Occasionally, claims have been made that pure *n*-paraffins have been isolated, but as this communication will show later, in one of these cases it is possible that the fractions were not pure *n*-paraffins.

Taking a moderate view, it seems reasonable to conclude that the methods employed have provided what may be termed concentrates of *n*-paraffin mixtures on the one hand, and non-normal concentrates on the other, the purity of which will naturally depend on the degree to which the resolution was taken. The reason for this deduction regarding composition is that it has been found that one set of concentrates approaches closely some of the properties observed for the pure synthetic *n*-paraffins (*e.g.*, in setting point compared with ultimate analysis, molecular weight, density, refractive index, X-ray properties, etc). There seems no reasonable doubt, therefore, that these concentrates may be characterized as "*n*-paraffin mixtures," and if the purification has been taken far enough, a fraction may be obtained which approaches a pure *n*-paraffin. None the less, a measure of doubt may remain as to whether the methods of separation imposed, or the physical tests employed, are always sensitive enough to separate *n*-paraffins from paraffins with very slight chain branchings (assuming the latter to exist in the wax).

The other set of concentrates differs markedly in properties from the pure *n*-paraffins (and therefore also the *n*-paraffin mixtures). Thus, this group is found to have a substantially higher molecular weight than a pure *n*-paraffin of the same setting point, a higher density, a higher refractive index, and often a higher viscosity; and it is much softer than a normal paraffin mixture of the same setting point. Ultimate analysis indicates that such concentrates are either paraffins, or a mixture of paraffins and *cyclo*paraffins. Therefore it is concluded that this set of concentrates may be considered as composed of branched chain, or cyclic-paraffins, or a mixture of both. Buchler and Graves[2] term these non-normal concentrates "soft waxes." The term is an excellent one since it implies the very real ignorance that exists regarding their composition and selects their most readily apparent difference compared with *n*-paraffins of the same setting point or molecular weight. It will, therefore, be used in this communication where the "non-normal concentrates" are meant.

Partial Resolution of the full range of Paraffin Waxes from Burma and Assam Crude Oils.

Much of the work discussed in this communication was based on a partial resolution of five commercial paraffin waxes covering the normal setting-point ranges of these products, and the results will now be described. Some of the properties of the five waxes employed are set forth in Table I.

TABLE I.

Properties of Commercial Waxes subjected to Resolution by Distillation and Recrystallization.

	Burma 95/100° F. Wax No. 1.	Burma 110/12° F. Wax No. 2.	Burma 125/30 Wax No. 3.	Burma 135/40 Wax No. 4.	Assam 145/50 Wax No. 5.
Setting point, °F	98·5	111·7	127·8	138·1	146·3
Sp. gr. at 65° C	0·770	0·777	0·777	0·779	0·781
Hardness (Ball):					
60° F	—	18·0	76·5	75·0	79·5
85° F	—	"Z"	19·0	49·5	55·7
Hardness (Cone):					
60° F	5·43	12·1	64·9	70·2	67·5
85° F	—	—	15·8	—	—
95° F	—	—	—	24·8	—
105° F	—	—	—	—	30·2

Note.—For description of Hardness Tests see later.
"Z" approaching zero.

The general method followed that of previous workers. Essentially it is based on two facts:

(*a*) The soft waxes have a substantially higher boiling point than the *n*-paraffins of the same setting point.
(*b*) The soft waxes, as a class, are more soluble in solvents than the *n*-paraffins.

The distillation effect, (*a*), appears to be the greater; that is to say, if a wax containing soft wax is distilled, then a substantial segregation of soft wax into the later fractions and the residue is achieved. If, on the other hand, the mixture is crystallized from solvents only a very partial separation is effected.

Now the solubility of the *n*-paraffins decreases substantially with rise of setting point (and therefore boiling point). Thus distillation produces fractions in which the difference between the solubilities of the soft wax and the *n*-paraffins is very much enhanced and this enables substantial segregation of the two classes to be effected by re-crystallization from solvents.

The five waxes were therefore first separately distilled under vacuum (for details see Fig. 2 and description) into eight 10 per cent fractions leaving a 20 per cent residue. These fractions were then examined as

regards specific gravity, it being taken that any enhancement of gravity might denote segregation of soft wax. The results are set forth graphically on Fig. 1. It will be noted that relatively high specific gravities are shown in each case by the later fractions and that such enhancements increase as the setting points of the original paraffin waxes decrease. These fractions, which are indicated by broken lines in the diagram, were re-crystal-

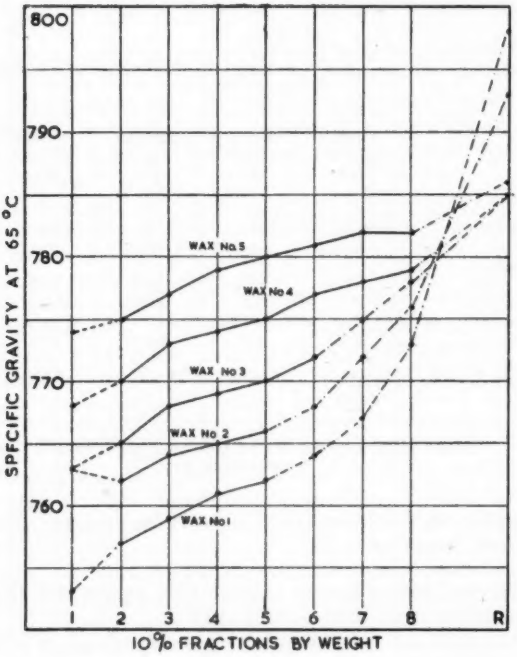

FIG. 1.

SPECIFIC GRAVITY AT 65° C OF FRACTIONS FROM DISTILLATION OF FIVE COMMERCIAL WAXES. BROKEN LINES INDICATE PRESENCE OF SOFT WAX.

lized from suitable solvents to separate the *n*-paraffins from the soft waxes (and any oil).

The fractions of more normal density (covered by the continuous lines), together with the *n*-paraffin concentrates separated from the soft wax-containing fractions, were bulked according to setting point and recrystallized from ethylene dichloride to give a range of fractions which tests show (for example Fig. 3) approximate to *n*-paraffin mixtures. The soft wax fractions were purified by recrystallization from either benzene, ethylene dichloride, or methyl ethyl ketone, bulked according to setting point, and filtered through silica gel. The details of this separation are set forth in Fig. 2 and appended working description.

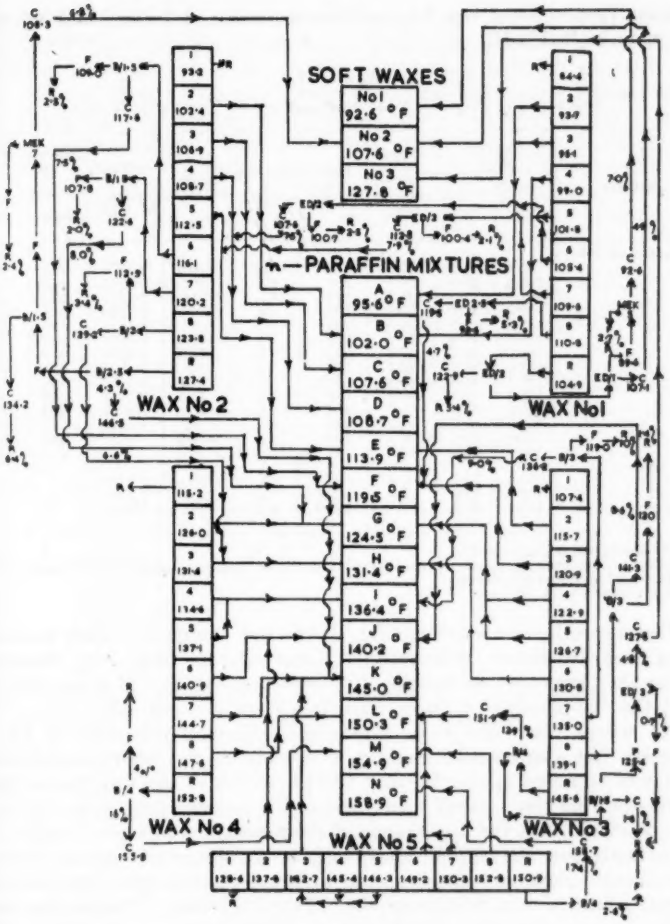

FIG. 2.

RESOLUTION OF FIVE COMMERCIAL WAXES FROM AN EASTERN CRUDE OIL INTO "n-PARAFFIN MIXTURE" AND "SOFT WAX CONCENTRATES".

Details of Procedures Described on Fig. 2.

(1) All temperatures in ° F where unspecified.
(2) Distillation in 5000-ml still; 3 ft 6 in column, 2 in diameter, filled with rings. Column lagged and electrically heated. Vacuum, below 2·5 cm.
(3) Fractions 10 per cent by weight; residue 20 per cent.
(4) Purification :

B	Benzene,
ED	Ethylene dichloride,
MEK	Methyl ethyl ketone.

B/1½=1½ parts benzene to 1 part of fraction.

[*Note: continued on p.* 546

Some properties of the "*n*-paraffin mixtures" and the "soft waxes" are given in Table II.

TABLE II.

Properties of Prepared "n-Paraffin Mixtures" and Soft Waxes.

Mixture.	Setting point.		Transition point (inverse rate), ° C.	Molecular weight.	Nearest *n*-paraffin	Density, 65°/4° C.	Refractive index, 60° C/D.[c]	Hardness[d] at 60° F.	
	° F.	° C.						Ball.	Cone.
n-Paraffin mixture:									
A	95·6	95·4	15·8	262[b]	C_{20}	0·7607	1·4278	10·4	9·14
B	102·0	38·9	20·6	288	C_{21}	0·7621	1·4293	48·8	37·6
C	107·6	42·0	25·2	299	C_{21}	0·7645	1·4303	53·0	62·6
D	108·7	42·6	25·9	302	C_{21}	0·7662	1·4309	54·5	52·3
E	113·9	45·5	29·6	323[b]	C_{23}	0·7683	1·4319	59·3	68·8
F	119·5	48·6	33·2	327	C_{23}	0·7705	1·4328	59·6	74·6
G	124·5	51·4	37·4	340	C_{24}	0·7728	1·4341	61·8	82·7
H	131·4	55·2	42·7	360	C_{25}	0·7753	1·4355	65·0	103·0
I	136·4	58·0	46·4	369[b]	C_{26}	0·7776	1·4367	103·9	155·0
J	140·2	60·1	49·6	386	C_{27}	0·7798	1·4373	106·2	146·0
K	145·0	62·8	52·6	404	C_{28}	0·7806	1·4387	94·3	142·0
L	150·3	65·7	55·7	422	C_{29}	0·7825	1·4399	74·5	124·0
M	154·8	68·2	58·5	438	C_{31}	0·7846	—	59·9	109·0
N	158·9	70·5	63·1	451[b]	C_{32}	0·7857	—	57·5	92·5
Soft waxes:									
No. 1	92·6	33·7	—[a]	422[b]	C_{30}	0·800	1·4468	—	—
No. 2	107·6	42·0	—[a]	423[b]	C_{30}	0·796	1·4461	—	—
No. 3	127·8	53·2	—[a]	452[b]	C_{32}	0·793	1·4443	—	—

[a] No observable transition point.
[b] Molecular weights by depression of freezing point (naphthalene) others calculated from setting point.
[c] Corrected to stated temperature.
[d] For hardness tests, see later.

The separation recorded on Fig. 2 was not complete. First fractions from each distillation were rejected; and oily fractions were discarded where they presented no feature of interest (see Fig. 2). It is not claimed that the "*n*-paraffin mixtures" are free from non-normals, or that the "soft waxes" are free from *n*-paraffins, although reference to Fig. 4 suggests that a substantial measure of segregation has been accomplished.

It will be noted (Table II) that the properties of the soft waxes differ markedly from the *n*-paraffin mixtures of the same setting point. It may also be stated that the appearance of the *n*-paraffins mixture is quite different both from the original waxes employed and the soft waxes, for they are all white, opaque, lustrous, and highly crystalline products, the low setting point fractions being composed of large crystals. The size decreases as the setting point rises. All fractions exhibit some measure of "crumbliness." The soft waxes are soft and transparent and there is no very evident crystallinity.

Percentage figures: Per cent by weight on wax charged.

F Filtrate,
C Crystals,
R Residue from distillation.

and Rejected from further purification.

Filtration temperatures, 60° to 65° F.

(5) Final purification of *n*-paraffin mixtures was by recrystallization of 1–4 parts of ethylene dichloride (depending on the setting point of the fraction) to one part of blended fractions.

Soft waxes finished by filtration through 30 to 60 mesh/in silica gel.

Reference to Fig. 2 demonstrates that the soft waxes were resolved from the lower setting-point paraffins. This is due to the refining methods employed in separating these waxes from the wax distillate whereby the slack waxes, from which the waxes were sweated, were obtained at a descending series of temperatures. Thus, since soft waxes have a relatively high solubility (in the oil medium), they tend to be concentrated in the slack waxes separated at the lower pressing temperatures. Sweating also works in the same direction, for sweats contain not only oil but also the more soluble waxes, and these are resweated with the appropriate

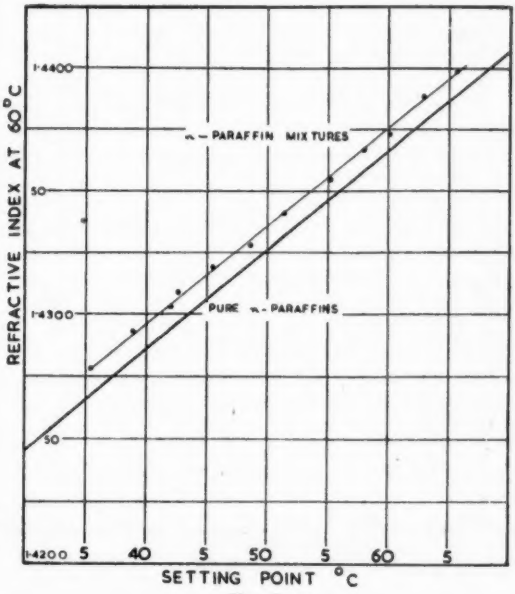

FIG. 3.

COMPARISON OF REFRACTIVE INDICES AT 60° C OF PURE-*n*-PARAFFINS WITH THE PREPARED "*n*-PARAFFIN MIXTURES".

intermediates from lower sweating-point scales. Indeed, it is as a rule found that soft waxes tend to be concentrated in the lower-setting-point commercial paraffin waxes.

The quantity balance from the resolution indicates that the purified waxes separated from the five commercial paraffins contain about 3·3 per cent by weight of soft wax (Fig. 2), and although the separation was not complete, it is considered that little error will arise if it is taken that the soft wax concentrates of the combined five paraffins amount to from 3 to 4 per cent by weight; but, as has already been pointed out, these are mainly concentrated in paraffins No. 1, 2, and 3.

Table II shows that the setting points of the *n*-paraffin mixtures range from 35·4° to 70·5° C and the molecular weights indicate that the *n*-paraffins

present appear to run from C_{20} to C_{32}. Since, however, first fractions were rejected from further purification, *n*-paraffins below C_{20} will be present in these waxes. Further, C_{32} marks the mean molecular weight of the last fraction ("N") and it is therefore practically certain that *n*-paraffins over C_{32} occur in this fraction. Therefore it may be approximately estimated that *n*-paraffins from, say, about C_{17} to C_{34} exist in the combined commercial paraffins from these sources. Speaking generally, this

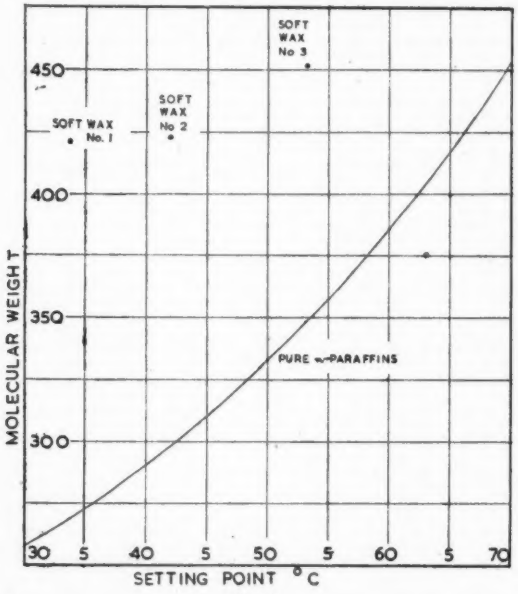

FIG. 4.

COMPARISON OF MOLECULAR WEIGHTS OF THE SOFT WAX CONCENTRATES WITH *n*-PARAFFINS.

may also be taken as the approximate range occurring in ordinary commercial paraffins (compare, for example, Buchler and Graves).[2] The molecular weight of the soft waxes indicates that the hydrocarbons comprising them are in the neighbourhood of C_{30} to C_{32}.

Summarizing, it may therefore be concluded that ordinary commercial paraffin wax consists of preponderating quantities of *n*-paraffins, ranging roughly from C_{17} to C_{34} and substantially smaller quantities of non-normals, which, in the case quoted (paraffins from eastern crude oils), appear to be in the neighbourhood of C_{30} to C_{32}, and amount to some 3 to 4 per cent by weight of the total commercial paraffins (ranging in mean setting point from 98·5° to 146·3° F).

Some Solid State Properties of the Pure *n*-Paraffins.

Now the commercial value of petroleum waxes arises, in practically every application, as a result of their properties and behaviour in the solid state. Therefore any account of such properties must be formulated against the background of such knowledge as exists on the solid-state behaviour of the pure *n*-paraffins which, as has been pointed out above, occur in preponderating quantity at least as far as the commercial paraffin waxes are concerned. Since, in any case, very little knowledge exists on the properties of pure *n*-paraffins outside the paraffin wax range (over about C_{35} or so), the following discussion is perforce limited to this range.

In this connexion it is of some interest to consider briefly the relationship between melting point and molecular weight, or the number of carbon atoms. Much work has been devoted to this subject.[7-11] For the immediate purpose of this communication it will suffice to point out that for a given rise in melting point over the early part of the curve connecting melting point and the number of carbon atoms (say about the C_{17} range) a smaller number of the series is included than for the same rise at a later part of the curve (say over C_{34} range). This point has some bearing on the complexity in composition of commercial petroleum waxes of high setting point and will be taken up later.

The outstanding solid-state behaviour of the *n*-paraffin series arises, however, on account of their complicated polymorphism. It would be outside the scope of this communication to deal in detail with this fascinating and exceedingly complicated subject. It is hoped, however, that the following brief summary may be adequate for the present purpose.

Over the ranges which comprise commercial paraffin wax (C_{17} to C_{34} about) the solid *n*-paraffins may exist in one of four distinct modifications depending on the individual, the temperature at which it is examined, or the method of preparation.[12-17]

Thus, near the melting point, all paraffins over this range exist in a closely packed hexagonal form, which Müller likens to closely packed hexagonal pencils.[12] Because X-ray examination shows that the long axes of the paraffin chain are perpendicular to the plane containing the ends of the molecule this form may be referred to as a "vertical form."

In this form, which is stated to be transparent, the molecules are free to rotate about their long axes. In view of a certain confusion that appears to exist on the nomenclature of the *n*-paraffin polymorphs, this form will be termed the "transparent, vertically rotating form."

As cooling proceeds, a transition point is reached where the transparent, vertically rotating form changes into one of two alternative forms. First, the freedom of rotation disappears and a form is produced which is opaque. It may be referred to as the "opaque non-rotating vertical form." However, the loss of freedom of rotation may be immediately followed by the long axes of the chains tilting relative to the plane containing the chain ends. This produces a third form, which may be called the "opaque (non-rotating) tilted form."

It is stated that the odd members of the series do not exhibit the opaque tilted form.

The transitions "transparent vertically rotating form" to either "opaque, non-rotating vertical," or "opaque tilted" are reversible.

From C_{26} onward the paraffins can exist in a fourth form with a more highly tilted chain, but it appears that this form has only been observed in crystals obtained from solvents and not from melts or by transition.

This survey probably tends to oversimplify the mass of recorded facts. For example, Yatabe,[18] Müller,[12] and Kolvoort [19] note that C_{24} behaves somewhat differently from other near (even) members. Seyer, Patterson,

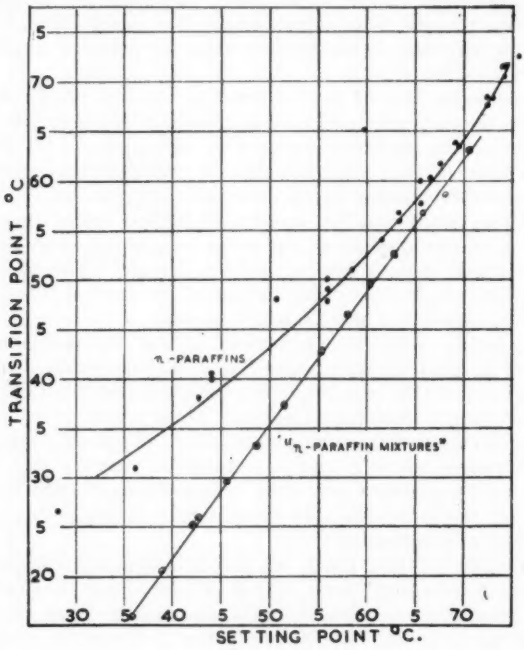

FIG. 5.

TRANSITION POINTS OF P-NORMAL PARAFFINS AND THE *n*-PARAFFIN MIXTURES *v.* SETTING POINT.

and Keays [20] remark that C_{30} does not quite conform to the general pattern of the even members.

Transition from one form to another causes various measurable changes in other physical (and probably mechanical) properties. It should first be noted that the change from the high- to the low-temperature stable forms takes place at a fixed transition point. Such transition points have been recorded by numerous investigators.[7, 13, 14, 20]

Fig. 5 displays these results as an approximate relationship between the melting point and the transition point over the ranges occurring in paraffin wax. It will be seen that as the number of carbon atoms in the molecule increase the transition point approaches the melting point.

Thus, *n*-paraffins over about C_{36} should show no transition. Gray [10] takes the view that above C_{36} the opaque, non-rotating, vertical form is stable at the setting point.

Now the transition point is much more sensitive to impurities (such as other *n*-paraffins and other paraffins) than the setting point and has for this reason been employed as a method of testing purity.[14] It will be similarly used later in this communication.

Transition on cooling is accompanied by an evolution of heat (heat of transition). Therefore the total latent heat evolved on cooling from above the setting point to a temperature below the transition point of the high- to low-temperature stable forms is comprised both of the latent heat of fusion and the heat of transition. In Table III, collected results of latent

TABLE III.

Heats of Fusion and Transition for certain pure n-*Paraffins.*

No. of carbon atoms.	Molecular weight.	Melting point, °C.	Heat of fusion, etc., to low-temperature stable form, cal/g.	Heat of fusion to high-temperature stable form, cal/g.	Heat of transition (by difference), cal/g.	Refs.
22	310	44·5	59·92	37·69	22·23	7
24	338	51·1	60·8	39·8	21·0	19
26	366	56·6	61·16	38·32	22·84	7
30	422	66·0	59·57	38·93	20·64	7
34	478	72·8	63·93	39·94	24·04	7
35	492	74·6	61·86	41·92	19·94	7

heats of fusion and transition are given. It will be noted that the total latent heat down to the low-temperature stable forms runs from about 59 cal/g for the lowest (even) *n*-paraffins occurring in the paraffin-wax range to about 64 cal/g for the highest. The latent heat for the only available odd member (C_{35}) appears to be somewhat lower (62 cal/g) than even members of corresponding molecular weight.

The latent heat of fusion itself (*i.e.*, to the high-temperature stable form) similarly ranges from 38 to 40 cal/g for the even members of this range, and, for C_{35}, is 42 cal/g. As shown in Table III this gives heats of transition of a mean value of about 22 cal/g for the even members. C_{35} has a heat of transition 19·9 cal/g. It may be said that these figures lend some support to the results from X-ray examination in that they indicate the losses in freedom of movement, may be somewhat different for the even than for the odd members of the series, and may be related to the adoption by the members of either the opaque vertical, or the opaque tilted form.

It will be apparent from the above that the heat of transition is a substantial proportion of the total latent heat for the pure *n*-paraffins.

Transition affects physical properties such as the coefficient of expansion (and density), variations in solubility, and electrical and mechanical properties.

The Occurrence of Polymorphism in Paraffin Waxes and Purified Fractions Therefrom and its Effect on Certain Physical Properties.

A substantial volume of work shows the effect of transition on various physical properties of commercial paraffin waxes and purified fractions therefrom. Thus, Carpenter,[21] as a result of studies including microscopic examinations, solubility, and coefficients of expansion, came to the conclusion that paraffin waxes had a transition point some 15° C below their setting points. Yannaquis,[22] came to a similar conclusion as the result of microscopic studies of purified wax fractions.

Scott Harley,[23] working with commercial paraffin waxes and purified fractions therefrom, noted a transition by microscopic and thermometric methods in certain instances. This investigator, however, drew attention to the important fact that in a good many samples and prepared blends no transition was observable either microscopically or thermometrically. He also notes that waxes possessing a definite translucency do not give evidence of transition, but waxes that are opaque are usually associated with a marked transition effect. He also suggests that waxes which do not exhibit a transition change are likely to be more homogeneous in structure with temperature variation than those waxes which show transition.

Lord [24] describes a method of plotting results from the cooling curves of paraffin waxes and purified fractions therefrom, that enables the effect of heat of transition on the cooling curve to be used as a method of evaluating the mean transition point of some commercial paraffin waxes. This method, known as the "Inverse Rate Method," has been previously used for determining transition points in metals.

Scott Harley notes that the (mean) transition points of commercial paraffin waxes and purified fractions therefrom are substantially below those of the *n*-paraffins of the same setting point, and Lord observes the transition points of commercial paraffins and purified fractions therefrom increase with their purity.

Both Scott Harley and Lord suggest that the development of mottling that takes place on the cooling of many commercial paraffin-wax melts is due to air being expelled from the high-temperature stable form when it changes to the low-temperature stable form. Scott Harley further points out that microscopic examination suggests that the low-temperature stable form is more dense than the high and that the change is accompanied by a considerable contraction. Lord is inclined to associate the cracks which develop in certain commercial paraffin waxes on cooling to a similar cause.

Use may be made of the above observations to express the relative purity of waxes regarding their hydrocarbon composition. For example, Fig. 5 plots the transition points (determined by the method described by Lord) of the *n*-paraffin mixture described on Fig. 2 and detailed on Table II on the same figures as those of the *n*-paraffins. It will be observed that the transition points of the *n*-paraffin mixtures are substantially below those of the pure *n*-paraffins of the same setting point. Similarly, Fig. 6 shows the values of the transition points of certain commercial paraffin waxes of Eastern origin against their setting points. In this case the transition

points of the commercial paraffin waxes are even further below those of the *n*-paraffins.

As the complexity of the wax mixture increases, so does the distinctness with which the transition point may be thermometrically observed decrease. In this respect transition point is similar to setting point, but the transition point is much more sensitive in the sense that whilst, for a certain wax, no transition point may be observable by any thermometric method yet employed, yet the setting point may still be relatively sharp. Thus, for a highly purified mixture, the transition point is very sharp and quite

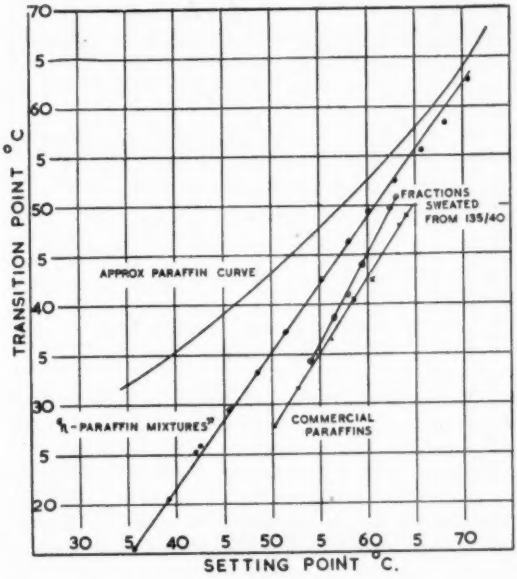

FIG. 6.

TRANSITION POINTS OF PURE *n*-PARAFFINS, COMMERCIAL WAXES, AND PURIFIED FRACTIONS THEREFROM *v.* SETTING POINT.

definite (as evaluated by the method described by Lord); for some few commercial paraffin waxes, a much less sharp point may be found; for a good many, the "point" appears as no more than a slight roundness. These three cases are illustrated in Fig. 7. With a large number of commercial paraffin waxes, however, no transition point (or range) is observable by any thermometric method so far employed.

The question therefore arises as to whether the transition range is so wide that the heat changes are too spread out to be observable, or whether transition does not occur or, at most, only partially. This possibility is of some importance because if no transition occurs, or at any rate only to a partial extent, then some or all of the *n*-paraffins the commercial paraffin waxes contain may exist in the high-temperature stable form at ordinary

room temperatures, and it is likely that this will effect certain of the physical properties of such waxes.

A consideration of latent heats of fusion of commercial paraffin waxes (measured down to normal room temperatures) throws some light on this point. It will be recalled that the latent heat of fusion (*i.e.*, to the high-

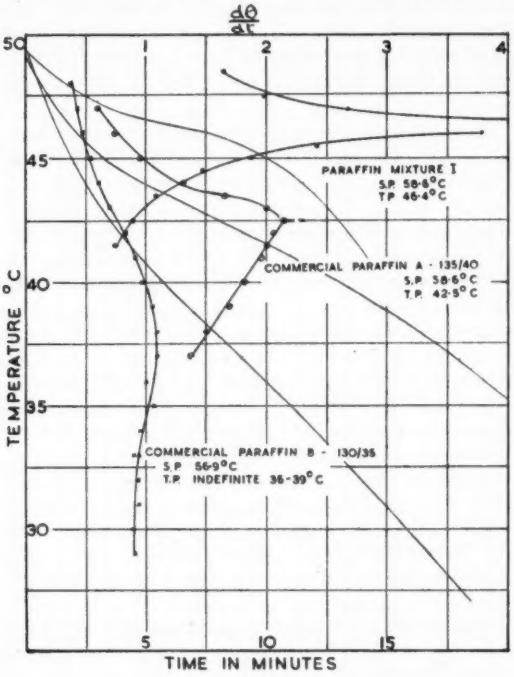

FIG. 7.

TRANSITION POINT BY INVERSE RATE METHOD SHOWING DEGREE OF VARIATION IN SHARPNESS OF THE TRANSITION EFFECT.

temperature stable form) has a mean value of about 40 cal/g for the *n*-paraffins occurring over the paraffin-wax range, and that the total latent heat down to the low-temperature stable forms is about 60 cal/g. Table IV

TABLE IV.

Heats of Fusion of some Commercial Waxes.

S.P., ° C.	Latent heat of fusion (to room temp), cal/g.	Ref.
51·7	40·3	25
52·2	38·9	26
52·4	35·1	27
65·3	43·8	26

gives the latent heats of some commercial paraffins down to room temperatures—that is to the temperature at which the low-temperature stable form exists in the case of the pure *n*-paraffins.

It will be observed that in no case is the latent heat of fusion much in excess of 40 cal/g, and in some cases it is lower. Thus in these cases, which are believed to be fairly representative, it would not be unreasonable to conclude that the bulk of the *n*-paraffins they contain remain in the high-temperature stable form at ordinary (room) temperatures. It is, of course, also likely that some of the commercial waxes examined contained soft waxes which may depress the heats of fusion.

Further, Parks and Todd [28] give the latent heats of fusion to the low-temperature stable form of three highly purified wax fractions obtained by Buchler and Graves, which were considered to be pure, or nearly pure, C_{20}, C_{25}, C_{33}. The results are given in Table V.

TABLE V.

Latent Heats of Fusion of C_{20}, C_{25}, C_{33}, obtained by Buchler and Graves, from Petroleum.

No. of C atoms.	S.P., ° C.	Latent heat of fusion to low-temp. form, cal/g.	Ref.
20	36·4	52·0	
25	53·3	53·6	28
33	71·1	54·0	

Again the values of the heats of fusion are substantially below those of the pure *n*-paraffins and it is difficult to resist the conclusion that, in all probability, the three fractions cannot be pure *n*-paraffins, but mixtures thereof. It seems not unreasonable to suggest that it might prove helpful to examine fractions isolated from petroleum, and thought to be pure *n*-paraffins, regarding their transition points or latent heats of fusion. This should enable some assessment of their purity to be made.

The facts discussed above appear to favour the view that, for commercial waxes, the change of the *n*-paraffins they contain from the high- to the low-temperature stable forms is only partial, and in most cases takes place only to a limited extent. It will be recalled that the high-temperature stable form is the "transparent, vertically rotating form." It has been pointed out that this form has some properties similar to those of liquid crystals.[29, 30, 31] It may be that the relative freedom of molecular movement of this form confers on the melt a certain measure of flexibility (or semi-fluidity) and translucency at ordinary room temperatures. Scott Harley's [23] remarks on the translucency and opacity of commercial paraffin waxes should be noted in this connexion. Thus, quite apart from any effects conferred by soft waxes, commercial paraffin waxes may vary in properties simply on account of variations in the relative properties of the polymorphic forms.

Finally, under this head, the variations in certain electrical properties of solid waxes should be noted.

Thus Willis Jackson [32] has explored the D.C. conductivity of certain

commercial paraffin waxes and purified fractions therefrom. He noted abnormalities in the changes of conductivity with temperature variations between room temperatures and the molten condition. Such abnormalities show maximum variation over the ranges at which thermometrically observed transitions take place. It is concluded that the abnormal behaviour is due to transition effects.

From quite other considerations Willis Jackson [33] has shown that to describe the behaviour of a cetyl palmitate solution in a high-setting-point paraffin wax when subjected to a high frequency field, it is necessary to assume that the paraffin has, in the solid state, an "internal viscosity" approximately the same as that which would be exhibited by the liquid paraffin at the same temperature. Fuoss,[34] discussing the internal properties of polymers, quotes this work of Willis Jackson as supporting the view that micromolecular zones of the paraffin used exhibit certain characteristics of the non-crystalline condition. This highly suggestive idea will be discussed later.

The Mechanical Testing of Petroleum Waxes.

Up to this point the subject matter has been confined to the composition of petroleum waxes and a discussion of their physical properties. In matters of utilization, however, it is probably correct to say that most interest attaches to their mechanical properties. Even a superficial examination of waxes indicates large qualitative differences between waxes in such properties as crumbliness, plasticity, hardness, and rate of softening with temperature rise, and it is not unreasonable to assume that tests measuring the variation of such properties are likely to prove informative. It is presumably for this reason that mechanical tests on wax have been described.

Thus Carpenter [21] gives a test for the breaking strength of paraffin. Seyer and Inouye [35] developed a method for determining the tensile strength of paraffin.

Espach [36] describes a method of conducting tensile-strength tests on commercial paraffin waxes using a Perkins Tensile Tester. This test has been used for routine control and investigational purposes. It is shown that the tensile strength of paraffin wax is extremely sensitive to the presence of oil and other impurities. It is claimed that the test gives useful information regarding the behaviour of commercial paraffin waxes in application. (See also Padgett and Killingsworth.[47])

The A.S.T.M. Penetration Test is coming into fairly general use for the testing of petrolatum and ceresin types of petroleum waxes. It has not found acceptance for testing commercial grades of paraffin, probably because it gives variable results with these products. This is considered to be due to the fact that the progress of the fine needle into the wax mass is much affected by the heterogeneity of the melt.

Hardness Testing of Petroleum Waxes.

Tests Employed.

Since 1931 the author of this communication has devoted some study to the development of hardness testing of waxes and the interpretation

of the variations in hardness in terms of variations in wax composition. The tests employed are described in detail in the Appendix.

Two tests have been devised, known as the Ball and the Cone hardness. They have certain features in common; thus a specific weight of wax is melted in a container of specific size and cooled under specified conditions. The melt is then transferred to a water bath held within $\pm 0{\cdot}25°$ F at the test temperature for 30 minutes in the case of routine testing. The penetration is then performed by contacting the indentation piece with the wax, and then applying the load in such a manner that the full load is smoothly reached after 5 seconds. Six impressions are made, and the hardness number calculated as the quotient of the load applied in kilograms, and the area of the impression produced. This gives the "hardness number," which in physical terms is the weight in kg/sq.cm. acting on the sample at the moment the test finishes. Thus this test is similar in all important essentials to the Brinell test as applied to metals.

In the case of the ball hardness test, a $\frac{1}{2}$-in metal ball is employed at a load of 6·5 kg. The diameter of the impression made is measured and the mean of the six readings taken. (Tables converting diameter of impression to hardness numbers are employed.) This test has been employed for the routine testing of wax products since 1934. It is conducted at two temperatures, namely, 60° F and 85° F.

Ball hardness numbers run from not more than 90 down to under 20 for commercial paraffin waxes tested at 60° F, depending mainly on the oil content of the wax, the setting point, and the composition. This will be discussed further below. The ball hardness at 85° F is always substantially less than that at 60° F, and runs from about 60 down to below about 5 (below which the test no longer functions since, at this point, the depth of penetration of the ball is equal to its radius).

The ball hardness test is more sensitive to variations in oil content than the Cone hardness, and for this reason has been preferred for routine testing. It has two faults: first, the diameter of the impression is not always easy to measure precisely, and second, at relatively low temperatures the ball penetrates the wax to a distance equal to the radius of the ball, thus limiting the ranges of temperatures over which the test may be applied.

The cone hardness test employs a 60° cone, which is blunted to specified conditions. Special devices require to be employed whereby the relatively sharp tip of the cone is contacted with the wax as nearly as possible under no load. The present apparatus has a contacting load of about 1 g. The load applied is usually 1·5 kg and the depth of penetration is measured by a suitable scale attached to the rod carrying the penetrating cone.

As before, the area of the impression is calculated, and from this, the hardness number.

The cone hardness test is employed at present mainly for research and investigation. It enables a study of the variation of hardness with temperature to be made over relatively wide temperature ranges, and is a generally more adaptable test for investigational purposes. Both tests are subject to a probable error of ± 2 per cent.

The ball and cone hardness numbers of the same wax differ. Generally, the cone hardness number is lower in the case of commercial paraffin

waxes. This difference is thought to be due to the fact that the ball test is somewhat more compressive, and the cone test is somewhat more shearing, in nature.

The Effect of Oil on Hardness and Hardness–Temperature Curves.

Before discussing the results of hardness testing in terms of composition of petroleum waxes a few matters of general interest must be considered.

It is already known that tensile strength is sensitive to small variations in oil content,[36] and hardness is similarly sensitive and probably also all

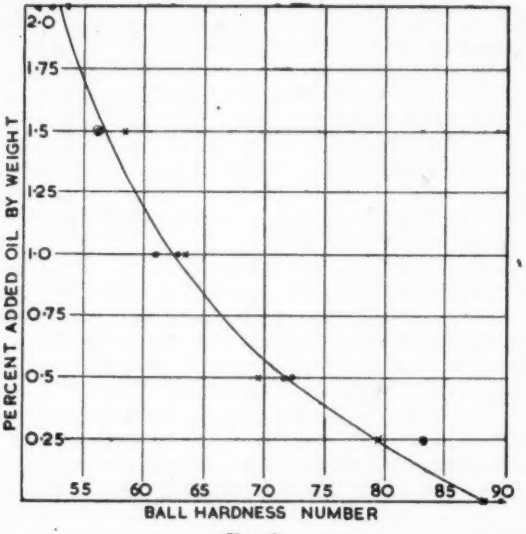

Fig. 8.

VARIATION OF BALL HARDNESS AT 60° F WITH OIL CONTENT FOR THREE OIL-FREE WAXES.

other mechanical tests. As has been stated above, the ball hardness is more sensitive than the cone hardness, and for this reason data is given for the effect of variation of oil content on ball hardness on Fig. 8.

Three commercial paraffin waxes of differing setting point were acid treated and then subjected to intensive sweating. From these sweatings fractions were selected that were considered to be substantially oil free. Table VI details some properties of these waxes.[37] Mixtures of these waxes with known weight percentages of the oil normally associated with them were prepared. The results are plotted on Fig. 8. It will be seen that a curve may be averaged through the plots. It is apparent from this curve that 0·25 per cent of oil reduces the ball hardness at 60° F from about 88 to 79, and that 1 per cent of oil reduces the hardness to about 62. The sensitivity of hardness to the presence of oil is thus evident. Further, providing the stock, and the general methods of processing remain unaltered, ball hardness at 60° F can be employed as a method of oil

TABLE VI.

Properties of "Oil-free Waxes" used for investigating the Effect of Oil on Ball Hardness at 60° F.

Origin of wax.	Setting point, ° F.	% yield by weight of "oil free" fraction.	Setting point of fraction. ° F.	Ball hardness at 60° F.
125/30 Burma . .	127·9	60	128·9	88·1
135/40 ,, . .	138·3	30	140·5	89·6
135/40 Assam . .	137·3	55	137·7	88·1

determination from 0 to 2 per cent of oil, for, as will be seen from the examples quoted (Table VI and Fig. 8) a setting-point variation from 127·9° to 140·5 F in the wax makes no very evident difference to the results obtained. The method is not generally applicable, however, because the hardness of oil-free commercial paraffin waxes varies both with the source and the method of processing.

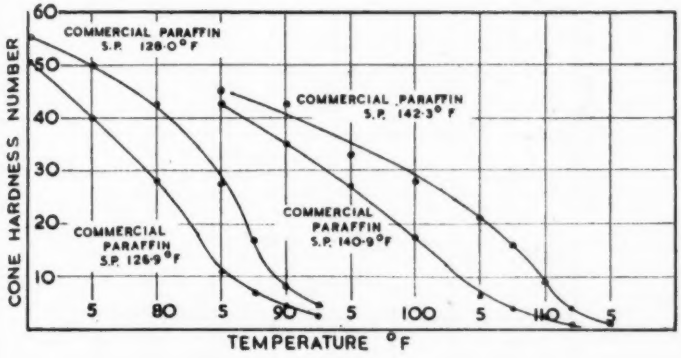

FIG. 9.

CONE HARDNESS TEMPERATURE CURVES OF FOUR COMMERCIAL WAXES.

None the less, those interested in the determination of oil in wax, might well consider the possibility of the employment of mechanical tests for the assessment of the effect of oil. It should be noted that hardness (and other mechanical tests) are most sensitive to variations of small quantities of oil (under say 0·4 per cent). Thus, where oil-extraction methods become difficult or indefinite and lack in sensitivity, a mechanical test is most sensitive. Moreover, consideration might be given to the proposition that it is not the oil content that is of practical importance, but the effect that such oil has on the solid-state properties of the wax.

It is interesting to consider that a description of the large effect of small variations in oil content on mechanical properties would be that such oil is held on the surface of crystal masses and aggregates and thus lubricates the slip. The facts do not favour any view suggesting the oil is

tightly held by the wax—that is, in the case of the ordinary commercial paraffin waxes at present under discussion.

The second matter of general interest is the hardness–temperature curves of waxes. For this purpose, the cone hardness is employed and some typical results are given on Fig. 9. It is a matter of no surprise that wax should soften with temperature rise, and general qualitative experience with waxes suggests such softening would be fairly rapid. The curves suggest, however, that in some cases the rate of softening is very

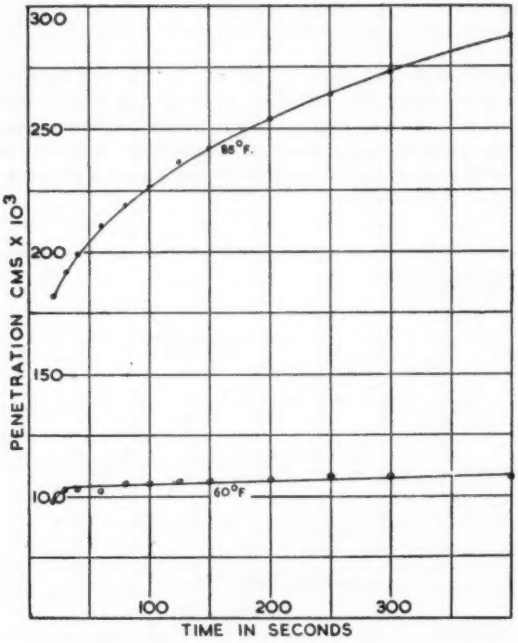

FIG. 10.

INCREASE OF PENETRATION OF CONE WITH TIME FOR COMMERCIAL 125/30 WAX AT 60° AND 85° F.

high. Thus the two 125/30 grades have a cone hardness of over 50 at 70° F, and, some 20 to 25° F higher, the hardness has fallen to 2·5. In both cases, the waxes are still 30° to 40° F below their setting points. Evidently, if some degree of hardness were required in the wax in its utilization, then these waxes would probably not be very suitable at temperatures much above 90° F (that is below temperatures that might be experienced in hot weather). Further, the change in the direction slope of the curves should be noted. It is typical of all waxes so far tested and is suggestive of incipient phase changes in the mass.

In this connexion it is illuminating to study the progress of penetration of the cone into the wax mass. This is shown on Fig. 10. These results

were obtained by permitting the load to act for 400 seconds on a 125/30 wax at 60° F and at 85° F. At 60° F there is a very slow increase in penetration with time: at 85° F the rate of penetration is much higher, indicating that a substantially greater fluidity appears to have developed for a rise of 25° F, again favouring the view that there may be some kind of phase changes occurring at temperatures some 45° F or so below the melting point.

Evidently a description of these values and changes in terms of composition is likely to prove a matter of some complexity.

In an endeavour to offer some explanation, the hardness properties of the *n*-paraffin mixtures, the soft waxes, and blends therefrom will first be described.

The Hardness of *n*-Paraffin Mixtures.

Fig. 11 gives the plot of cone hardness values of the *n*-paraffin mixtures at 60° F against their setting points. It will be seen that there is a very

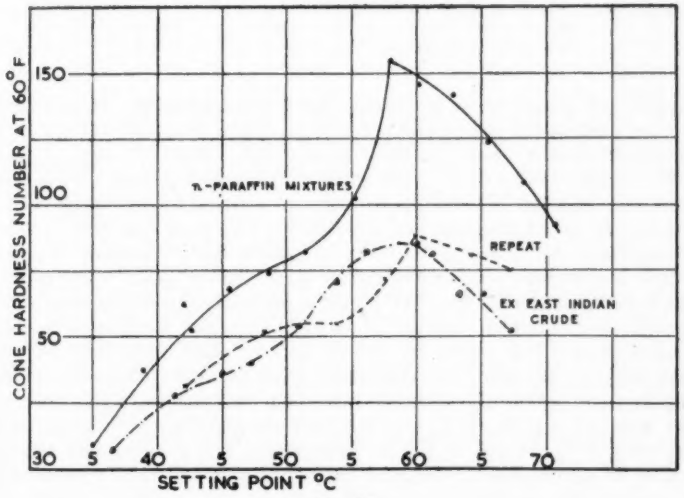

Fig. 11.

CONE HARDNESS AT 60° F OF *n*-PARAFFIN MIXTURES.

well-developed maximum on the curve in the neighbourhood of a S.P. of 58° C (136·4° F). This result may be characterized as unexpected since there is no *a priori* reason known to the author why *n*-paraffin mixtures which are steadily increasing in molecular weight should develop a maximum of this kind. Initially, therefore, the results were suspect. The work was repeated first with waxes from the same source and secondly with waxes from another crude oil. In these two cases, a smaller and less efficient distillation equipment was employed. None the less, as Fig. 11 indicates, the fractions again show that a maximum develops over about

the same setting-point ranges. To obtain still further evidence commercial paraffin waxes from Scottish shale oil and Iranian crude oil were distilled in the larger and more efficient still and the fractions of setting points covering the peak hardness ranges selected and recrystallized. The results obtained are given in Table VII.

TABLE VII.

Cone Hardness at 60° F of "n-Paraffin Mixtures" over the Peak Hardness Ranges from Burma, Assam, Iranian, and Scottish Shale Oil.

Source of "*n*-Paraffin Mixture."	S.P., ° C.	Hardness at 60° F.	
		Cone.	Ball.
Mixture I } From Burma and Assam	58·0	155·0	103·9
" J } Waxes	60·1	146·0	100·2
" M }	68·2	109·0	59·9
Scottish Fraction 7C } Separation of soft	58·7	124·0	87·9
" " 8C } wax and re-	61·3	142·0	108·7
" " RC } crystallization	66·8	86·5	74·0
Iranian Wax 7C } Separation of soft	57·6	146·0	93·1
" " 8C } wax and re-	59·6	121·0	74·0
" " RC } crystallization	62·2	109·0	61·4

Again the occurrence of the maximum is demonstrated. It may therefore be stated that purified *n*-paraffin mixtures from all sources so far examined show a peak hardness over a S.P. range of approximately 57·6° C (135·7° F) to 61·5° C (142·5° F), and it appears not unreasonable to suggest that this is a definite property of *n*-paraffinic mixtures.

It will be noted that one characteristic of this peak hardness is that it develops and increases as the wax is progressively purified. Thus an oil-free commercial wax of about the same setting point will possess a cone hardness of about 70 at 60° F, the moderately purified fractions have a hardness of about 90, and the more highly purified fractions a hardness of about 150. This might be considered consistent with the view that some impurity was being concentrated in peak-hardness fractions. Against this, however, must be considered the fact that the *n*-paraffin mixtures over these ranges (H, I, J, and K) show no abnormality in liquid-state properties or in general crystalline appearance, and also the fact that the method of purification would lead one to suppose that the concentration of any impurity would lower and not increase the hardness. Further, it would be surprising if waxes from four different crude oils all contained the same type of "impurity." On balance, therefore, the more plausible view is that the peak hardness is due to a property of *n*-paraffin mixtures which develops on purification; and, probably, therefore, is to be associated with the polymorphism of the *n*-paraffin series. The setting points covering the peak hardness range, namely, 57·5° to 61·5° C, correspond roughly with the *n*-paraffins from C_{26} to C_{30}. Now it may or may not be pertinent to the present discussion to recall that from C_{26} on, it is stated that the even *n*-paraffins can exist in a fourth, opaque, more highly tilted form. If, however, the effect is due to polymorphism it would not be unreasonable to expect that the hardness above the transition point

(that is, when the low-temperature stable forms have passed to high-temperature stable form) should show no peak but a smooth development of hardness, since, as far as is known, the high-temperature stable form of the *n*-paraffins is the same over the ranges under consideration. Unfortunately it is difficult to test this conclusion, because the transition point of the *n*-paraffin mixtures rises for the high-setting-point fractions to temperatures at which the low-setting-point fractions are too soft to test. Some data is, however, presented in Table VIII.

TABLE VIII.

Cone Hardness of "n-Paraffin Mixtures" in the Transition Zones.

	n-Paraffin mixture.			
	H.	I.	J.	M.
Transition pt., ° F . . .	108·9	115·5	121·3	145·6
Cone hardness :				
60° F	103	155	146	142
105° F	16·4	34·5	38·2	31·8
110° F	3·06	23·5	34·1	28·4
115° F	—	6·98	24·5	26·0
120° F	—	—	7·5	25·3

Although the results are by no means conclusive, they appear to suggest that the position of the peak hardness, relative to setting point varies with the test temperature when the test temperatures are in the transition zones, and these facts are not unfavourable to the view expressed, namely, the development of the peak hardness on purification is probably related to the polymorphism of the *n*-paraffins.

Consideration has been given to the possibility that the fractions exhibiting peak hardness do so simply on account of the fact that they are, for some not very apparent reason, more highly purified than the others and thus undergo a greater proportion of transition to the low-temperature stable form, which, being the harder form (see later) causes the increase. It would be expected, however, if such were the case, that the transition points of the peak hardness fractions would show a definite rise over the other fractions, since, as has already been pointed out, this property is most sensitive to purification and rises with the degree of purity. No such rise is evident.

It should be noted that in spite of the high hardness exhibited at 60° F by the "peak fraction," the melt is highly crystalline, would almost certainly be termed "crumbly," and it is doubtful if such fractions would have a high tensile strength.

The development of peak hardness over a limited setting-point range appears to result from purification, and it does not therefore follow that commercial waxes will be hardest (at room temperatures) when they have setting points within the peak hardness ranges. Actual experience with commercial waxes confirms this. Providing the oil contents of such waxes are substantially the same, there is no notable trend one way or the other over a setting-point range of about 122° to 150° F (cf., for example, the ball-hardness results recorded in Table VI).

It is not, therefore, considered probable that differences that arise in hardnesses of commercial paraffin waxes will be influenced by this factor, although it must be admitted that no decisive evidence on this point has so far been obtained.

Hardness of Soft Waxes compared with *n*-Paraffin Mixtures and Commercial Paraffin Waxes. Their Plasticizing Effect.

It will be recalled that Buchler and Greves[2] characterize the non-normal concentrates from petroleum waxes as "soft wax"; Fig. 12 provides some evidence for the justification of this term.

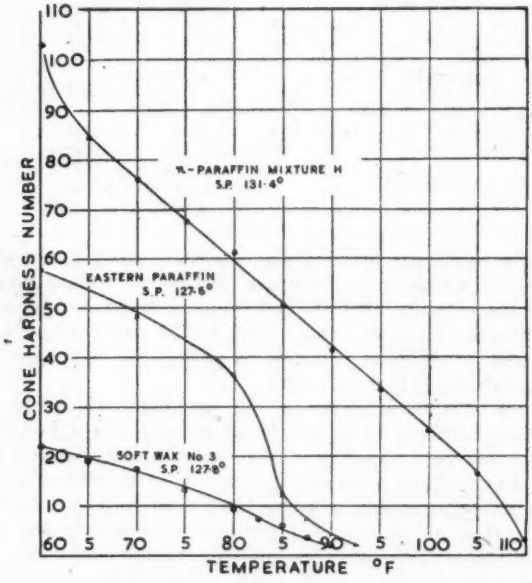

Fig. 12.

CONE HARDNESS TEMPERATURE CURVES OF A COMMERCIAL WAX, A *n*-PARAFFIN MIXTURE AND SOFT WAX NO. 3, ALL OF ABOUT THE SAME SETTING POINTS.

The figure compares three waxes of about the same setting point.

(*a*) a commercial paraffin wax 125/30 grade, S.P., 127·6° F.
(*b*) *n*-paraffin mixture H, S.P., 131·4° F.
(*c*) soft wax No. 3 (see Fig. 2 and Table II), S.P., 127·8° F.

It is evident that soft wax No. 3 is very much softer at all temperatures than the *n*-paraffin mixture of approximately the same setting point. Thus, at 60° F, the cone hardness of mixture H is 103, and of soft wax No. 3 is 22. Further, soft waxes No. 1 and 2 (Fig. 2, Table II) are less than 3 at 60° F. Thus, there is good justification for the term proposed by Buchler and Graves.

It will also be noted that soft wax No. 3 is considerably softer than a commercial paraffin wax of approximately the same setting point, and it is a simple step to draw the inference that the presence of soft wax in a suitable mixture of *n*-paraffins would exert a plasticizing effect on the latter which might well produce the type of curve exhibited by the commercial waxes.

Two further points, however, require to be considered.

Effect of Soft Waxes and Transition on the Hardness–Temperature Curve.

First, it is required to consider the possible effect of transition of *n*-paraffin mixtures from the low- to the high-temperature stable form.

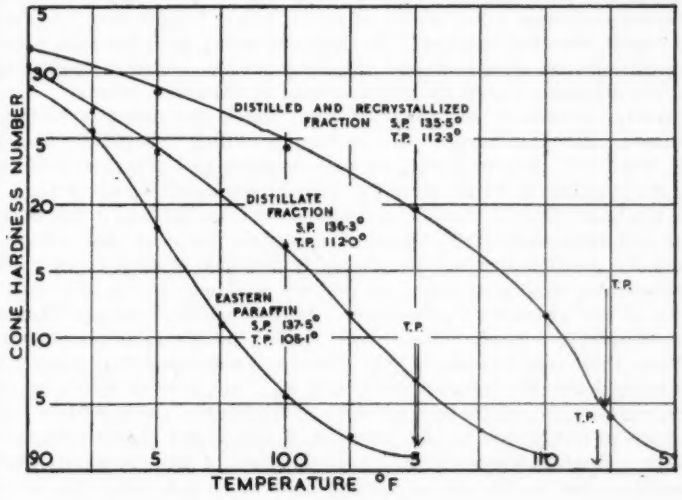

Fig. 13.

CONE HARDNESS TEMPERATURE CURVES OF THREE WAXES OF ABOUT THE SAME S.P. SHOWING THE EFFECT OF PURIFICATION ON THE SHAPE OF THE CURVES AND ITS RELATIONSHIP TO THE THERMOMETRICALLY OBSERVED TRANSITION POINT.

It is reasonable to expect that the high-temperature stable form will be softer than the low-temperature stable form (at the same temperature), and that a transition from one form to the other for a mixture of *n*-paraffins might also produce the type of curve exhibited by commercial waxes. Thus, for example, the part of the curve covered by the temperatures between 5° and 92° F for the commercial wax, S.P. 128·0° F, on Fig. 9 might represent the high-temperature stable form hardness–temperature curve, and the curve covered by the temperature ranges between 60° and 80° F the low-temperature stable form curve.

Some elucidation on this point may be gained by a consideration of the data graphically displayed in Fig. 13. Thus, the thermometrically

observed transition point of the commercial wax (S.P. 137·5° F) is 105·1° F. It will be seen that this temperature is substantially higher than that required by the suggestion advanced above that zone of change of direction of slope of the curve may be due to transition effects. Therefore, in this case such changes in direction of slope is not likely to be mainly due to transition effects, and is more probably due to the effect of soft wax which the commercial wax is known to contain.

An endeavour was now made to produce a wax containing a higher concentration of soft wax. This was obtained by fractionally distilling a 125/30 grade commercial paraffin wax and selecting one of the later fractions (into which soft wax would be concentrated—see Figs. 1 and 2) of about the same setting point as the commercial wax. This fraction was de-oiled. It had a setting point of 136·3° F and a transition point of 112·0° F. Its hardness curve is given on Fig. 13. The thermometrically observed transition point occurs at a still higher temperature relative to the lowest recorded hardness. It therefore seems probable that when a wax mixture contains soft wax the shape of the hardness–temperature curve is determined more by soft wax than by transition effects.

Finally, a fraction was prepared from which the soft wax had been removed. For this purpose the fraction preceding "Distillate Fraction S.P. 136·3° F" was recrystallized from benzene and ethyline dichloride. It gave a product of setting point 135·5° F and a transition point of 112·3° F. The hardness curve is given in the same figure (Fig. 13), and it will be seen that the thermometrically observed transition point is now placed at about the position at which the change in direction of slope occurs. This demonstrates that transition can produce a change in the direction of slope in the absence of soft waxes. It also affords evidence that the high-temperature stable is softer than the low (at the same temperature).

From these observations it may therefore be deduced that, since most commercial paraffin waxes contain soft wax, the rate of softening with temperature rise, and the general slope of the hardness–temperature curve is more probably due to the presence of soft waxes than to transition effects. Further, where the change in direction of slope is mainly due to transition (due to the wax containing little or no soft wax), the relative position of this change will be somewhat nearer to the setting point. This effect is exhibited by the hardness–temperature curves of the two high-setting-point commercial paraffin waxes displayed on Fig. 9. In this case the wax S.P. 142·3° F can be shown by refractive-index consideration,[38] to contain little or no soft wax whilst the wax S.P. 140·9° F contains an appreciable amount.

In the main, however, it seems correct to deduce that the presence of soft wax has a sufficiently plasticizing effect on commercial paraffin waxes to cause relatively large variations in the mechanical property of hardness. The point is further demonstrated by the data given in Table IX and Fig. 14. Two blends from the *n*-paraffin mixtures were prepared to correspond to the 125/30 commercial wax grade. In the first, no soft wax was included, and the second contained the same blend with 10 per cent of soft wax. The plasticizing effect of the soft wax is evident.

It is also worth recording that the blend free from soft wax is in no way distinguishable in appearance, or any normal test, from commercial

TABLE IX.

Blends matching 125/30 Commercial Waxes blended from n-Paraffin Mixtures and Soft Waxes.

	125/30 with no soft wax.	125/30 with 10% soft wax No. 1.
Composition, per cent weight of fraction :		
Soft wax No. 1	—	10
n-Paraffin mixture C	10	9
" " D	10	9
" " F	10	9
" " G	20	18
" " H	10	9
" " I	10	9
" " J	10	9
" " K	20	18
Setting point, ° F	127·8	127·6
Ball hardness :		
60° F	84·3	66·8
85° F	28·6	14·2

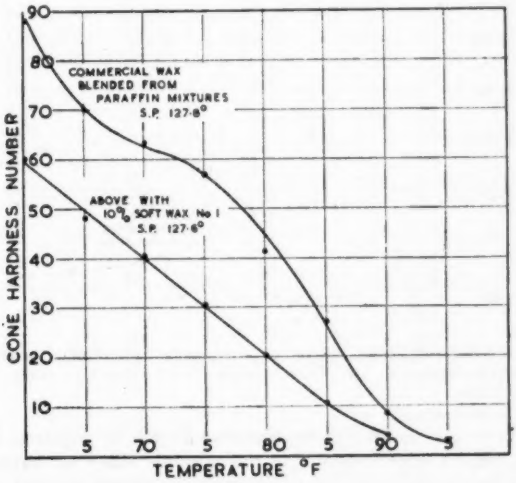

FIG. 14.

CONE HARDNESS TEMPERATURE CURVES OF A "COMMERCIAL" WAX BLENDED FROM THE n-PARAFFIN MIXTURES AND SAME BLEND PLUS 10 PER CENT OF SOFT WAX NO. 1.

paraffin waxes. No evidence has ever been obtained suggesting that soft wax is an essential ingredient of an acceptable commercial wax.

POSSIBLE EFFECT OF THE VARIATIONS IN THE PROPORTIONS OF HIGH- AND LOW-TEMPERATURE STABLE FORMS OF THE *n*-PARAFFINS IN COMMERCIAL PARAFFIN WAXES ON HARDNESS.

Second, it is required to consider the conclusion reached earlier that probably most commercial paraffin waxes consist of mixtures of high- and

low-temperature stable forms at ordinary room temperatures, in which the high-temperature stable form exists in preponderating quantities, together with the deduction made immediately above that the high-temperature stable form is softer than the low at the same temperature.

The point is further illustrated in Fig. 15. In this case sufficient of the high-temperature stable form curve is available to enable a very rough extrapolation to be made to the lower temperature. If this form could exist, or be made to exist, at 40° F then the curve strongly suggests that it would be substantially softer than the low-temperature stable form at the same temperature.

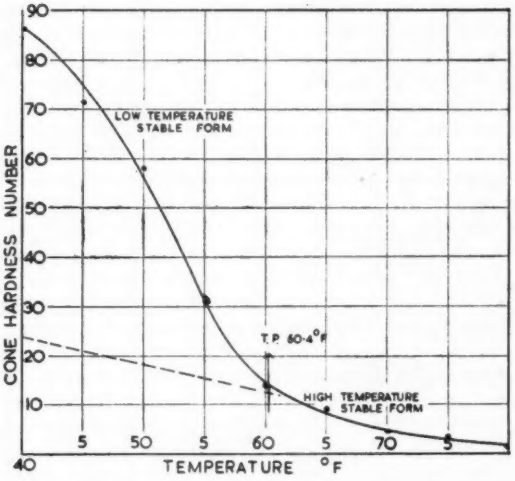

FIG. 15.

CONE HARDNESS TEMPERATURE CURVE OF *n*-PARAFFIN MIXTURE A, GIVING APPROXIMATE EXTRAPOLATION OF HIGH-TEMPERATURE STABLE FORM TO LOWER TEMPERATURES.

Clearly, however, more experimental evidence is required before any conclusions can be drawn regarding the possible effect on hardness of the variation in the proportions of the two forms in the case of commercial paraffin waxes. Experimentally the possibility is not at all easy to examine, for it is difficult to exclude the interfering effects that may be conferred either by varying proportions of soft wax in different commercial paraffin waxes on the one hand, or the possible effect of varying proportions of peak hardness fractions of the *n*-paraffin mixtures on the other.

These considerations suggest that it would be desirable to attempt to vary the proportions of the high- and low-temperature stable forms at room temperatures in the same wax, for only by some such means can it be certain that any observed variations in hardness are not due, either wholly or in part, to changes in composition.

However, by again following the experimental techniques employed in the study of metals, it is possible to obtain some information on this

subject. Thus, if a solidifying wax is held at a range of temperatures downward from the setting point and then " quenched " by sudden cooling in a bath held at, say, 60° F, it is probable that when the temperature from which the quenching is made is above the transition point, the high-temperature stable form will be " frozen " in the melt and will therefore exist in greater quantity at 60° F (for a time at any rate) than if the melt were normally cooled to the same temperature. Further, as the temperatures from which the quenching is made vary, so should, presumably, the ratio of the high- to the low-temperature stable forms.

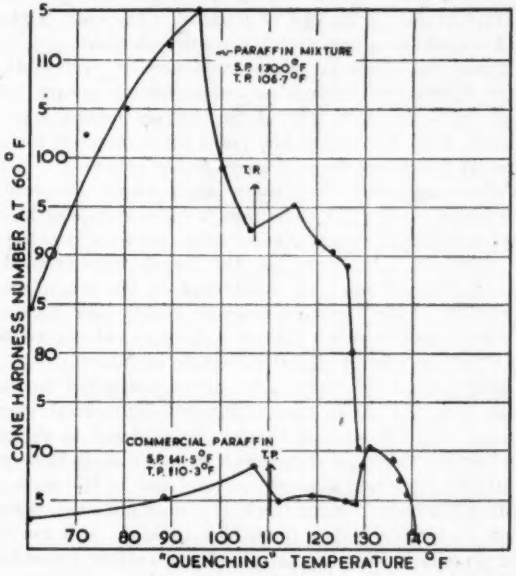

FIG. 16.

EFFECT OF " QUENCHING " FROM ELEVATED TEMPERATURES ON CONE HARDNESS AT 60° F.

Fig. 16 illustrates the experimental results obtained from such an investigation. Two waxes were chosen for the test; one a *n*-paraffin mixture, and the other, a commercial paraffin wax showing a fairly well-defined (thermometrically observed) transition point. They were both held for two hours at various temperatures below their setting points and then " quenched " by sudden immersion in a bath held at 60° F. The hardness determination was made after 30 minutes.

The results show systematic variations, and substantial ones in the case of the *n*-paraffin mixture.

It cannot be stated, of course, that these changes must be due to varying proportions of high- and low-temperature stable forms, but it is suggested that the arguments in favour of this interpretation are strong.

(1) It has already been shown that there is little doubt that the high- is

softer than the low-temperature stable form of the *n*-paraffins at the same temperature. Therefore, if quenching at temperatures near the setting point (*i.e.*, well above the transition point) " freezes " the high-temperature stable form in the melt, such melts should be softer than those obtained by normal cooling. The results are in line with this conclusion.

(2) It has already been reasonably conclusively demonstrated that a *n*-paraffin mixture undergoes substantially more transition than a commercial paraffin wax. It is therefore to be expected that a *n*-paraffin mixture should show more variation than a commercial paraffin wax because the possible extent of the variations in the proportions of the high- to the low-temperature stable forms will be greater in the case of the *n*-paraffin mixture. This again is in line with the results obtained.

(3) The variations observed show evidence of systematic variation relative to the thermometrically observed transition points, and therefore appear to be in some way related to the phenomenon of transition. Transition itself, however, marks the point (or a range in the cases under consideration) at which one form changes to the other.

It is therefore suggested that, taken as a whole, the results are not unfavourable to the view that variations in proportions of high- and low-temperature stable forms present at room temperature affects the mechanical property of hardness. However, in the cases considered the effect is evidently a complicated one. It would not be correct to state that an increased quantity of the high-temperature stable form necessarily has a plasticising effect on the melt. There is strong evidence to suggest that a hardening effect may be produced in certain instances.

These results cannot, of course, be directly applied to variations in hardness that occur in melts from different commercial paraffin waxes normally cooled to 60° F because there is no evidence to suggest that the two cases are comparable; for example, it appears likely that quenching at high temperatures may well alter the crystal size in the melt, and this in itself may affect hardness. None the less, it does not seem unreasonable to conclude that variations in the quantities of high- and low-temperature stable forms present in commercial paraffin waxes at room temperatures probably affect the mechanical property of hardness and that increasing quantities of the high-temperature stable form will not necessarily confer a softening or plasticising effect.

Summary of Conclusions on Hardness Testing.

Summarizing the data and conclusions reached on the property of hardness, it may be concluded:

(1) That, in common with other mechanical tests, the property of hardness is much reduced by the presence of even small quantities of oil. It is suggested that the oil occurs on the surfaces of the crystal masses thus lubricating the slip.

(2) Wax hardness falls rapidly with rise of temperature, reaching a very low figure at temperatures some 30° to 40° F below the setting points. Hardness temperature curves show changes in direction of slope towards the higher temperatures of testing. It is suggested that

this is due to incipient phase changes that take place over these temperature ranges and may occur some 45° F or so below the setting point.

(3) The cone and ball hardness at 60° F of the *n*-paraffin mixtures shows a well defined maximum over a temperature range from 56·0° C to 61·5° C (133° F to 143° F). Further evidence indicates that this is a general property of such mixtures from whatever source. It is suggested that the development of the peak, which becomes more pronounced on purification, arises on account of the polymorphism of the *n*-paraffins; and the suggestion is made that it may be due to the highly tilted opaque form which is said to develop from C_{26} onward. It is not considered probable that this effect develops in commercial paraffin waxes, but no conclusive evidence on this point can be offered.

(4) Soft waxes are shown to be very much softer than either *n*-paraffin mixtures or commercial paraffin waxes of the same setting point.

(5) It is shown that the zone of change in direction of slope of the hardness–temperature curves occurs at a temperature below the thermometrically observed transition point in a commercial paraffin wax and that an increase in the soft wax concentration decreases the temperature at which the hardness of the wax reaches its lowest observable value. It is concluded that in the case of most commercial paraffin waxes the zone of rapid softening is probably mainly due to the presence of soft waxes and not to transition effects.

(6) It is shown that when soft waxes are removed from a wax mixture, the point of change in direction of slope occurs at about the thermometrically observed transition point. It is concluded that when commercial paraffin waxes contain no, or little, soft wax, the change in direction of slope is due to transition effects, and that, in this case, the zone will be at a somewhat higher temperature than when soft wax is present.

(7) The plasticizing effect of soft wax is shown by the preparation of mixtures matching commercial products, one of which contains soft wax, whilst the other does not.

(8) Evidence is adduced which indicates that the high-temperature stable form is softer than the low at the same temperature. Evidence is also known which indicates that commercial paraffin waxes contain preponderating quantities of the high-temperature stable form at room temperatures. Evidence is given which suggests that variations in the high–low-temperature stable form ratios probably affects the hardness of commercial paraffin waxes in a complicated manner. It does not seem to be by any means invariable that the presence of the high-temperature stable form should soften the wax.

The Variations in Hardness and Hardness–Temperature Curves with Changes in Wax Composition.

The following suggestions can thus be advanced describing the mechanical property of hardness in terms of the composition of commercial paraffin waxes and their physical properties.

First, it seems evident that, at a given temperature, the hardness of a wax is determined by a variety of complicated factors. It is partly determined by the quantity of oil present. It is partly determined by the range of *n*-paraffins present, for, even if the "peak" effect noted for *n*-paraffins mixture does not show itself in commercial paraffins, the hardness of the *n*-paraffins themselves (being, for example, harder than the soft waxes), will help to determine the actual magnitude of the number. It is partly determined by the presence of soft wax, which, as far as is known, always has a softening or plasticizing effect. It is probably also partly determined by the ratio of high- to low-temperature stable forms co-existing in intimate admixture at the temperature in question, and this ratio in turn is dependant on the "purity" or width of cut of the commercial paraffin wax, an increase in cut making for larger proportions of the high-temperature stable form. It is not surprising in the circumstances that commercial paraffin waxes from various sources, even when they contain the same quantities of oil and have the same setting points, show large and superficially inexplicable variations in hardness.

Secondly, the form of the hardness–temperature curve appears to be determined by a variety of complicated factors, for not only do the hardness properties of the components change in what might be termed a natural way due, say, to simple expansion effects, and possibly the alteration of the ratio of the high- to the low-temperature stable forms, but also such evidence that exists makes it almost impossible to resist the conclusion that what has previously been termed incipient phases changes occur at temperatures very much below the setting point of the wax. It must not be forgotten, of course, that the so-called setting point is a mean value, or that resolution of a commercial wax of say 127·9° F S.P. yields small fractions of S.P. about 90° F or even lower. It is difficult to believe, however, that such components are all sorted out together when solidification occurs so that they melt in the normal manner when their setting points are reached. It is far more probable that there will be a purely random distribution of chain lengths.

Further, it has been deduced that the shape of the curve, particularly over the zone of most rapid softening, is mainly effected by the presence of soft wax. Here again the term "soft wax" covers a wide range of individuals some of which probably have a setting point even below room temperatures. Again, it has also been demonstrated that, in the absence of soft wax, commercial paraffin may show a zone of rapid softening due to the transition effects of the *n*-paraffins. Once more such transition almost certainly does not occur at a point, but occurs over a range of temperatures.

Now it is known that oil causes a fall in hardness; but it would be far too facile to assume that the liquid content rises as temperature advances due to the individuals comprising the wax liquifying when their melting point is reached, and that this describes the manner in which hardness falls with temperature rise. It is suggested that it is more probable that all commercial paraffin waxes are mainly comprised at normal temperature of crystal zones, but that "amorphous" zones also occur which increase in quantity, and fluidity as the temperature rises. This view will be more fully developed in the final summary.

Petroleum Ceresins and Petrolatum Waxes.

(*Note.*—The term "Petroleum Ceresins" will be applied to the hard, brittle, high setting point waxes, and "Petrolatum Waxes" will be applied to the softer, tougher and stickier waxes usually of somewhat lower setting point than the petroleum ceresins.[38])

As an approximate generalization it may be stated that the petroleum ceresins and the petrolatum waxes and those products which consist of a natural admixture of both are won from fractions of higher boiling ranges than wax distillates (from which commercial paraffin waxes are separated) or from distillation residues. The difference between such waxes and commercial paraffin waxes is very marked.[39] Table X compares the hardness properties of representative samples.

Table X.

Hardness Properties of Paraffin Waxes, Petrolatum Waxes, Petroleum Ceresins, and Others.

Wax.	Setting pt, ° F.	Cone hardness at 60° F.
Paraffin wax 106/8	107·9	6·37
„ „ 125/30	128·0	73·1
„ „ 145/50	146·2	67·5
Petrolatum waxes :		
"Micro-crystalline No. 1"	157·5	6·9
„ „ No. 2"	185·0	50·6
„ „ No. 3"	142·3	32·3
Refined Polish ozokerite	—	32·8
Petroleum ceresin No. 1	185·0	138·0
„ „ No. 2	176·4	118·0
Sucker rod (Burma) wax	200·1	236·0
"Z" wax (German I.G. synthetic)	222·1	265·0

Note.—Sucker-rod wax and German "Z" wax included as they are stated to be mainly *n*-paraffinic in composition.

Broadly speaking it may be considered that the individuals comprising petrolatum waxes and petroleum ceresins start at about the point where the individuals comprising commercial paraffin waxes finish. Further, it is not unreasonable on *a priori* grounds to assume that both the *n*-paraffins and the non-normals continue into these waxes and that the petroleum ceresins represent concentrations of *n*-paraffins, whilst the petrolatum waxes represent similar types of hydrocarbons, but of higher molecular weight, to the soft wax present in paraffin wax. It should be recalled, in this connexion, that soft waxes have a higher boiling point than *n*-paraffins of the same setting point and, just as on distillation of a paraffin wax, the soft wax tends to be concentrated in the later fractions and the distillation residue, so will concentrates of the same types of hydrocarbons, but of higher molecular weight, tend to be concentrated in the later fractions and distillation residues of the crude oil.

It is much more difficult, however, to subject these waxes to the same type of resolution as may be applied to the commercial paraffin waxes. Thus they retain oil much more tenaciously and since the presence of oil increases, for example, both the refractive index and the density, it cannot

always be taken that high values in these properties represent concentrations of non-normal paraffins.

TABLE XI.

Refractive Indices of Microcrystalline (Amorphous) Waxes compared with n-*Paraffins.*[40]

Wax.	S.P., ° F.	Oil, per cent.	Refractive index at 80° C.	Nearest *n*-paraffin at 80° C.
Micro wax :				
Dark amber . .	145·4	1·26–1·56	1·4491	C_{33}/1·4301[41]
White . . .	146·2	0·66–0·93	1·4451	C_{33}/1·4308[41]
Standard oil syncera .	146·4	0·88–1·06	1·4330	—
Aristo	160·4	2·53–2·55	1·4362	C_{33}/1·4332[41]

Correction for temperature employed = 0·0004 per deg C.

However, the examples given in Table XI may be taken as tending to confirm the view that when such waxes are of low oil content, some waxes exhibit refractive indices substantially higher than those exhibited by *n*-paraffins of the same setting point.

TABLE XII.

Densities of Petroleum Ceresins and other Waxes at their Setting Points.

Wax.	S.P., ° F.	Density, S.P./4° C.	Cone hardness at 60° F.
" Z " wax (I.G. synthetic) .	222·1	0·786	265·0
Sucker rod (Burma) . . .	200·2	0·793	236·0
Petroleum ceresin No. 1 . .	183·0	0·787	138·0
" " No. 2 . .	173·4	0·797	118·0
" Microcrystalline " (petrolatum wax)	110·0	0·834	1·53
Density of *n*-paraffin S.P./4° (correction used 0·0007 per deg C	—	0·780 approx.	—

Similarly Table XII indicates that the densities of the petroleum ceresins suggest that they represent a concentration of *n*-paraffins. In particular it may be noted that the synthetic " Z " wax has a density approaching that of the *n*-paraffin (of the same setting point). Further it will be evident that the trend is for the hardness to rise as the density falls; which would suggest that high hardness probably denotes a preponderance of *n*-paraffins.

In this connexion, the results of a hardness method of examination are of some interest.

For a 60° cone, the relationship between the applied load, P (in kg), and the depth of penetration, h (in cm), may be written :

$$P = \frac{2}{3} h^2 H_c$$

where H_c is the cone hardness.

According to the investigations of Meyer [42] on metals, this may be written :

$$P^n = ah^2$$

which gives a as a constant for all values of P, and, in this case n is a constant depending on the material. Thus, also,

$$\log h = K + \frac{n}{2} \log P,$$

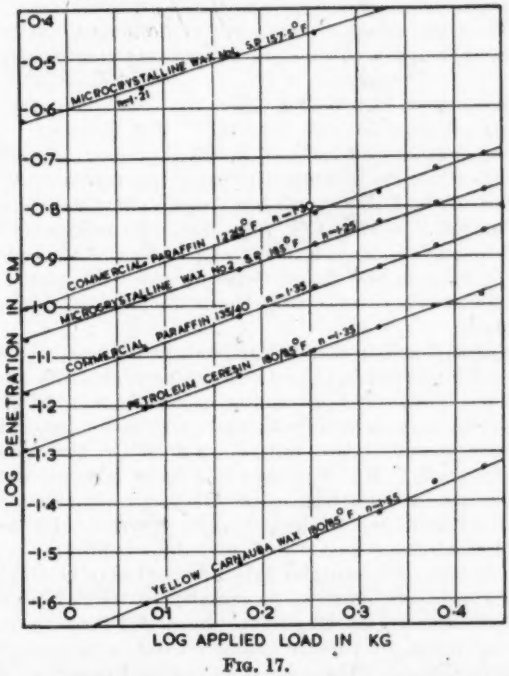

FIG. 17.

EFFECT OF INCREASING APPLIED LOAD ON CONE PENETRATION OF VARIOUS WAXES. DETERMINATION OF THE HARDNESS "n" INDEX AT 60° F.

and, if this form of Meyer's Law (originally applied to metals) also applies to waxes, then the plot of $\log h$ against $\log P$ should be linear, and the slope will be $\frac{n}{2}$, where the value of n depends on the nature of the material.

Fig. 17 gives the result of this procedure on two petrolatum waxes (microcrystalline waxes No. 1 and 2), a petroleum ceresin, two commercial paraffin waxes, and a yellow carnauba wax. The plots are linear and confirm to "Meyer's Law." Now examination shows that the slope of the curve is unaffected by the presence of oil (which, together with certain other factors such as width of cut, affects the value of K). All ordinary

commercial paraffin waxes, and purified fractions therefrom have a value of n (Hardness Index) from 1·33 to 1·35 at 60° F, setting point from 125° to 160° F. Commercial paraffin waxes containing much soft wax have somewhat lower values (1·30 to 1·33). Now it will be noted that the petroleum ceresin gives an index of 1·35 which is within the range found for all ordinary commercial paraffin waxes and purified fractions therefrom, whilst the petrolatum type of waxes have a lower index, being 1·2 and 1·24 for the two examined.

This evidence suggests that the petroleum ceresin in question is probably preponderatingly n-paraffinic in composition, whilst petrolatum waxes, giving a lower index value, are composed of a different "material."

Some interest attaches to the ranges of setting points comprising these products.

On account of their high boiling point, the distillation of these waxes is difficult with equipment normally available. For this reason, and following a suggestion of B. C. Allibone, a leaching method was developed for resolution. Leaching as a method of resolving petroleum products has been described. Also L. Ivanovsky has stated to the author in conversation that he employed it over thirty years ago. No originality is therefore claimed for the application of leaching as a method of resolution of waxes. It appears to be a powerful and elegant method of separation if some attention is given to details of construction of the apparatus and performance of the operation.

The method employed in the work to be described consisted in dispersing the wax on a comminutor in the ratio of not more than one part of wax to five parts of comminutor. Comminutors should be selected for the special purpose in view, and an excellent, non-active comminutor, is 30 to 60 mesh/inch porous pot of the variety employed in the manufacture of porous (electric) cells. If it is wished to achieve adsorptive resolution as well as resolution by variations in solubility, an adsorbtive comminutor such as silica gel (30 to 60 mesh/inch) may be preferred. The wax is melted into the comminutor and well stirred, and the dry mixture is poured into the leaching vessel. Any suitable type of vessel may be employed, but a large U-tube has been found a very useful pattern. The apparatus is then held at the selected leaching temperature, and the solvent, brought to the same temperature by passage through a coil in the same bath, is fed into the leaching vessel. The solvent and extract runs from the leaching vessel (the exit limb of the U-tube) to an extraction flask, where the solvent is evaporated and re-circulated. The extraction proceeds for a predetermined time at each extraction temperature, and the temperature is then raised and the operation repeated. Ethylene dichloride has been found the most useful solvent for non-adsorptive leachings, and the extraction temperatures employed may range from, say −20° C to temperatures just below the boiling point of the solvent. In this way, a series of fractions are obtained from the wax, which vary in setting point and other properties as the extraction temperature is advanced. Due, however, to the relative insolubility of very high-setting-point waxes (over about 200° F), it may be necessary to change the ethylene dichloride for a more powerful solvent (such as benzene or toluene) for the final extractions.

By using this method, the results displayed on Fig. 18 were obtained. The results of the resolution of four waxes are recorded.

(*a*) Microcrystalline wax No. 1 S.P. 157·5° F. This is a soft, sticky wax considered to be of the petrolatum wax type.

(*b*) Microcrystalline wax No. 2 S.P. 183° F. This is a type intermediate in properties between a petrolatum wax and a petroleum ceresin.

(*c*) A petroleum ceresin S.P. 183° F.

(*d*) A refined sucker-rod wax. This is from the same source as the wax examined by Carpenter [21] and reported by him to be mainly *n*-paraffinic in composition.

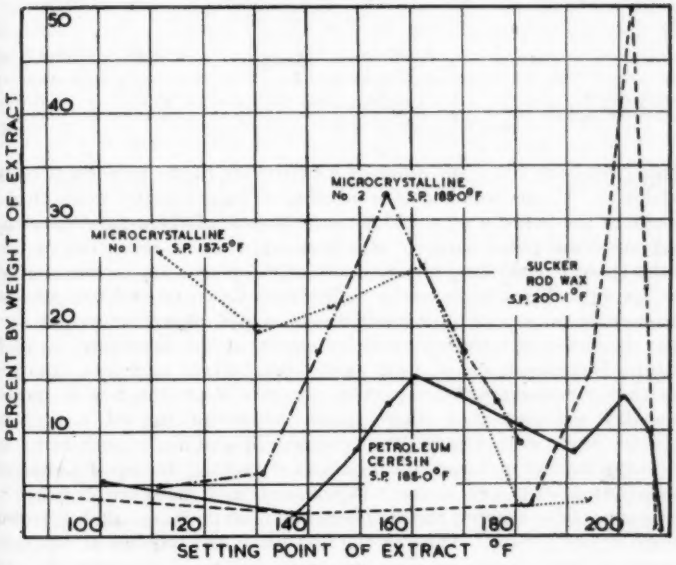

FIG. 18.

PARTIAL RESOLUTION BY LEACHING OF VARIOUS PETROLEUM WAXES WITH ETHYLENE DICHLORIDE AT INCREASING TEMPERATURE.

This figure indicates that the setting-point range of constituents is large. Thus the petroleum ceresin gives a range from about 100° C for its oily first fraction, to 208·3° F for its last fraction. Further, there is evidence that two maxima develop, one in the neighbourhood of 200° F and one at about 160° F. It is considered probable that the maximum at 200° F marks a concentration of high-setting-point *n*-paraffins (thus it has been considered probable that the sucker-rod wax is mainly *n*-paraffinic in composition).[21] The 160° F maximum is considered as most probably indicating a mixture of *n*-paraffin and soft waxes. Now it is of some interest to note that the first maximum (S.P 160° F,. say 70° C) would, if partly determined by the presence of *n*-paraffins, mark the presence of

approximately C_{32} to C_{33} which is about the point that it is estimated that the *n*-paraffins in commercial paraffin waxes finish. Similarly the setting point of the last fraction is 208·3° F (98° C), which would correspond to a *n*-paraffin of about C_{60} or so. It may therefore be approximately estimated that the *n*-paraffins present in the petroleum ceresin probably run from about C_{34} to C_{60}.

Table XIII summarizes this data in comparison with commercial paraffin waxes.

TABLE XIII.

n-Paraffin and Setting Point Ranges of Commercial Paraffin Waxes and a Petroleum Ceresin.

	Range of *n*-paraffins.		Ranges of S.P., ° C.	
	Members.	No. of members.	Overall.	Total range.
Paraffin wax . . .	C_{17}–C_{34}	18	21·0–72·3	51·3
Petroleum ceresin . .	C_{34}–C_{60}	27	70·0–100·0	30·0

Thus, although the main range of constituents in the petroleum ceresin is about 30° C, the number of *n*-paraffins is substantially more than in the case of the paraffin wax. This characteristic of the *n*-paraffin-setting-point curve was noted earlier. But it should thus be clear that not only are the chain lengths longer in the case of the petroleum ceresin, but also there are probably a large number of individuals crowded into a narrower setting-point range; including soft waxes of high molecular weight.

The discussion given above will indicate that the knowledge available regarding petroleum ceresin and petrolatum waxes is scanty compared with that possessed for the paraffin waxes. None the less it may be reasonably deduced that some general characteristics of composition apply for such waxes as for the commercial paraffins; that is to say, the former consist of *n*-paraffin mixtures of varying degree of complexity in association with soft waxes. Differences exist, however, between the two groups (classing for the moment petrolatum waxes and petroleum ceresins as one group). Thus, in the first place, the number of *n*-paraffins present appears, at any rate in some instances, to be considerably wider than the *n*-paraffins existing in commercial waxes. Thus, whilst commercial waxes may contain *n*-paraffins from C_{17} to C_{34}, petroleum ceresins may contain *n*-paraffins from C_{33} or so to roughly C_{60}. Thus, the petroleum ceresin probably contains *n*-paraffins which vary considerably more in chain length.

Further, due partly to the fact that non-normal waxes tend to be concentrated in heavy fractions and residues, and partly to the fact that in such products there is a much larger difference in solubility between soft waxes on the one hand, and normal paraffins on the other, it is possible to separate and find commercial use for the soft wax concentrates (or petrolatum waxes) from such heavy distillates and residues, whereas, as far as is known by the author of the communication, commercial waxes are natural mixtures of these components, and no special effort is made at commercial separation.

On the subject of polymorphism, as Gray points out, *n*-paraffins from about C_{37} upward should not exhibit transition of the type noted for the *n*-paraffins occurring in the paraffin waxes (*i.e.*, the transition point reaches the setting point at about C_{37}). Thus, speaking generally, complications due to the type of polymorphism occurring in paraffin waxes are likely to be of a small order for this group of waxes.

Gray suggests that the form stable at the setting point for *n*-paraffins C_{37} and upward may be the opaque vertical form. Whatever truth there may ultimately be found in this suggestion, it is certainly an observable fact that all high-setting-point waxes that appear to be mainly *n*-paraffinic in composition (*e.g.*, petroleum ceresins, sucker-rod wax, German "Z" wax, high-setting-point Fischer–Tropsch waxes) are all opaque at all temperatures after the solidification is complete. In this property they differ from the commercial paraffin waxes which are also mainly *n*-paraffinic but translucent in appearance. This then would describe the difference between the translucency of commercial paraffin waxes and high-setting-point waxes where *n*-paraffins also preponderate, in terms of changes in the possibilities of polymorphism with advancing molecular weight.

The Solidification of Petroleum Waxes—An Hypothesis.

Consider the solidification of a commercial paraffin wax free from soft waxes. It may be assumed that the *n*-paraffins comprising it will vary from approximately C_{17} to C_{34}. Thus, the lowest molecular-weight components are just half the chain length of the highest. Now according to Stewart [43] and Warren [44] in the case of the pure *n*-paraffins the hydrocarbons are "ranged" at temperatures just above their setting points; that is to say, small packets or groups of hydrocarbons lie with their long axes parallel in approximately the same positions as they will occupy in the form stable just below the setting point. It seems evident that since commercial paraffin waxes are substantially crystalline in structure, some similar kind of conditions must also exist for them at a similar temperature.

That some activity goes on at the surface of the liquid at temperatures near the setting point in the case of commercial paraffin waxes and purified fractions therefrom may be readily observed. For example, if a light powder be carefully sprinkled on the molten surface of such a wax so that it floats, then, as the wax cools, and at a temperature of approximately 2° F before any crystals appear, the particles of powder are propelled with surprising speed towards the sides of the container. Similarly, Fig. 19, indicates that the surface tension, determined by Sugden's method,[46] of various waxes, exhibits a maximum at about the same temperature relative to the first appearance of crystals in the solidifying liquid. These observations relate only to surface phenomena, but it is difficult to resist the conclusion that they are in some way related to some effect similar, say, to the ranging of molecules; that is to say, the molecules in the liquid taking up, to some extent, the more orderly arrangement that is characteristic of the solid state.

Obviously, however, there is one substantial difference between such ranging in the case of the pure *n*-paraffins on the one hand, and commercial paraffin waxes on the other. In the case of the pure *n*-paraffi n

all the chains are of the same length, in the case of commercial paraffin waxes, the chain lengths show considerable variation. In the absence of any evidence to the contrary, the most reasonable assumption would appear to be that the distribution of chain lengths throughout the mass of liquid at temperatures at which ranging occurs is random and remains random as complete solidification takes place. Thus, in an extreme case, a C_{34} chain may be partially ranged against a C_{17} chain. On solidification, therefore, it appears logical to conclude that greater or less proportions of certain of the hydrocarbon constituents are not held within any lattice. It is in fact suggested that micro-molecular zones develop which are, in all their strictly local properties, liquids (*cf.* Fuoss [34]), and further it is these which give rise to the low " internal viscosity " apparently necessary to describe the results obtained by Willis Jackson.[33]

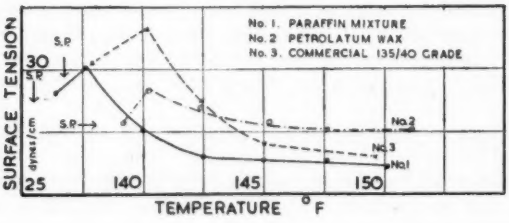

FIG. 19.

SURFACE TENSION OF PETROLEUM WAXES NEAR THEIR SETTING POINTS.

Now it is difficult to see how any transition from the high- to a low-temperature stable form can take place if there is a substantial disparity in the lengths of contiguous chains held in the partial lattice. Only portions of molecules will, in this case, even approximate to the true, fully developed, high-temperature stable form. Presumably, therefore, transition will only occur in those regions where, as a result of chance, chains of approximately the same length have ranged. This may, therefore, describe why only relatively small amounts of transition occur in commercial paraffin waxes, and why increase in the number of individuals comprising the wax tends in the direction of its complete suppression, as evidenced by no observable transition and low latent heats down to temperatures at which the low-temperature stable form should exist.

Thus, the picture suggested is one where a commercial wax (even when free from soft wax) is comprised of, perhaps, certain small macro-molecular zones where *n*-paraffins exist in the low-temperature form; but the bulk exist in a condition approximating to the high-temperature stable form; and, interspersed throughout the mass, micro-molecular zones which exhibit the characteristics of a " liquid," although different from a liquid in the sense that they are, as it were, anchored to other parts of the same molecule held in a lattice and therefore for the purposes of the discussion in the solid state. In this case, it would appear to be not inappropriate to term such zones " amorphous." Such micro-molecular zones would almost certainly contribute to the solid state properties of the wax, and they may be the cause of the general shape of the hardness–temperature

curve in the sense that temperature rise will, due to thermo-kinetic effects, tend in the direction of the increase of the volume of such zones (causing the "incipient phase changes" referred to earlier), at temperatures very much below the mean setting point of the wax.

If soft waxes are present the effects referred to above should be increased; for, presumably, those shorter portions of the *n*-paraffin chains contained in the branched chain or cyclic paraffins, will also range with portions of the chains of the *n*-paraffins; and this should tend in the direction of increase of the micro-molecular zones. This may describe why soft waxes are in fact soft; for in such instances the actual chain lengths ranged are likely to be shorter in length on the average than in *n*-paraffin mixtures or commercial paraffin waxes. Thus, the micro-molecular zones of "amorphous material" may well be much more extensive making for a much increased general "fluidity" or softness of the mass. On these grounds it would seem to follow that substantial resolution of a soft-wax concentrate into its components should tend in the direction of increased hardness and crystallinity.

It may be noted in passing that the account given above may possibly describe the phenomenon of "mal-crystallinity" noted by various investigators (*e.g.*, Ferris, Cowles, and Henderson).[3]

Since, as has been pointed out above, waxes from heavy distillates and crude-oil distillation residues contain an even wider range of *n*-paraffins crowded into a narrower setting-point range, and also often a higher concentration of soft wax, it is to be expected that this effect will be even more strongly developed in these products, although such mixtures should be substantially free from the complexities of that type of polymorphism known to exist for the *n*-paraffins present in commercial paraffin waxes. Moreover, whilst, when the chain lengths are not too different in length, it might be expected that the central portion of the chains are ranged, leaving the ends free, when the chain lengths vary widely (as they must do in such waxes, for not only do the chain lengths of the *n*-paraffins themselves vary more widely but also the mixtures usually contain greater proportions of more complex branched-chain and cyclic paraffins), the possibility exists that the micro-molecular zones of amorphous material exist internally within the chains and not only at the ends. Thus, for example, a long chain may have two or more sections of its chain ranged, but with unranged (*i.e.*, amorphous) zones in between. It should be noted that this condition is stated to exist in the case of many "polymers" and is apparently a phenomenon that naturally arises when the chain or molecule is long enough and the mixture is sufficiently complex.[45] Thus the horniness of polyethylene (which is stated to be comprised in the main of very long-chain paraffins) may be partly due to this cause. The molecules in the case of the petroleum ceresins and petrolatum waxes are, of course, very much shorter; but the mixtures are most complex, and it is suggested that they may mark the shortest chain lengths at which the phenomenon may occur.

Now it is well known that if wax distillates are taken too deeply into the crude oil they will prove difficult to press, and for this reason the fraction is as closely cut as possible to the point at which "amorphous" waxes enter the distillate. It would be consistent with the view expressed

to suggest that this is because at this point the total lengths of some of the *n*-paraffin chains, and the very wide differences in length, is sufficient for the development of such internal micro-molecular zones of non-crystallinity. It would seem reasonably evident that if oil molecules became " entangled " in such zones it would probably be of quite a different order of difficulty to disentangle them (and so effect the desired separation) than in the cases of a more normal wax distillate in which oil molecules were disposed at the ends of the crystalline portions of the chain. In one case the oil exists outside the crystalline portion of the wax, and in the other may be " entangled " within the wax molecule. And the same description would also apply to the very much greater difficulty in removing oil from petroleum ceresins or petrolatum waxes than from commercial paraffin waxes.

The suggestions advanced may also account for the difficulty experienced in finding a satisfactory terminology of these waxes. Thus they have been alternatively called " amorphous " or " microcrystalline." According to the suggestions made above, both terms might be considered correct, for the presence of both micro-molecular " amorphous " and " crystalline " zones is postulated; but since the zones may occur within the molecules the " crystallinity " is of quite a different kind from that met in simpler crystalline materials.

The above hypothesis of a solidification is offered with reserve because it is realized that the phenomena it endeavours to describe in somewhat more fundamental terms are most complex, and the evidence on which the hypothesis is based is far from complete. It is, therefore, offered in no sense as an explanation of the phenomena, or as anything approaching a theory. It is given in the hope that it may stimulate thought and discussion and possibly prove a point of departure for further studies by other workers.

In conclusion the author hereby records his thanks to the Directors of the Burmah Oil Co., Ltd., for their permission to present this paper. He also acknowledges, with gratitude, the help resulting from many stimulating conversations with Mr C. G. Gray, on the general subject of the solidification of petroleum waxes, and the assistance given by Messrs C. Kell and J. Parker who carried out much of the work herein described.

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APPENDIX.

I. The Ball-Hardness Test.

1. *Apparatus.*

The apparatus consists of a $\frac{3}{8}$-in metal ball (a phosphor-bronze ball bearing is preferred) which is contacted with the wax and a total load of 6·5 kg applied in the manner described below. In its simplest form the apparatus comprises :

(*a*) A $\frac{3}{8}$-in stainless-steel rod, cupped at one end to take the ball, and terminating at the other end in a circular platform covered by a disc of compressed cork. The total length of this rod may be, say, 12 in, and the platform 3 in in diameter.

(*b*) A $\frac{3}{8}$-in phosphor-bronze ball which may be attached to the cupped end of the rod by a soft bitumen.

(*c*) A suitable housing for the above, including a flat metal base plate to take the sample. The rod and platform are vertically and centrally mounted by, say, two bearings top and bottom. It is essential that the rod should give an easy sliding fit in the bearings.

(*d*) A weight which may be applied by hand to the platform. The total weight of ball, rod, and platform, plus the added weight should be 6·5 kg. The total weight of ball, rod, and platform should be not more than 350 g.

(*e*) A bath into which the machine (housing with base plate and rod assembly) may be placed, and which is large enough to contain the samples under test, together with stirrer and thermostatic controls. A suitable size of bath is 15 in × 10 in × 6 in deep.

2. *Preparation of the Specimen.*

Weigh 100 g of the sample to be tested into a circular nickel tray of the following dimensions :

Top internal diameter	4 in
Bottom internal diameter	3½ in
Internal height	1 to ¾ in
The thickness of the metal may be conveniently taken as	0·025 in

The tray thus has a slightly tapered side, permitting in most cases easy removal of the sample. Melt the sample on a boiling water bath, stir thoroughly, leave for ten minutes, then transfer the dish and contents and allow to cool for six to eight hours in air maintained at 55° to 60° F. The sample is then ready for test.

It should be noted that appreciable variation in the weight of sample taken may affect the result. Therefore a constant weight of wax (say 100 g) should be employed.

3. *Production of Indentations.*

A. *Indentations at 60° F.* Transfer the sample, which may be removed from the mould if preferred, or left therein if removal is difficult, to the water bath surrounding the bottom part of the machine. Maintain the temperature of the bath at 60° F $\pm$ 0·25° F. Allow the sample to remain in the bath for thirty minutes before the test is continued.

The impressions are now made on the surface formed at the wax–air interface.

To make an impression, place the tray on the base plate of the machine underneath the spindle carrying the ball, and lower the spindle carefully until the ball just makes contact with the sample. Gradually release the weight on to the platform so that the full weight is built up over a period of five seconds, and allow the full weight to act for a further thirty seconds. Thus the time from the first application of the weight to its final removal is thirty-five seconds. Remove the weight and lift the spindle. Repeat on different places on the surface of the wax until six impressions have been made. Three precautions must be observed in making these indentations :

(i) The sample should not rock on the base plate of the machine;

(ii) Care must be taken that no impression is made close to the curved contraction surface near the periphery of the sample;

(iii) Care should be taken that no solid particles are on the surface of the wax where impressions are likely to be made.

B. *Indentations at 85° F.* Raise the temperature of the water in the bath to 85° F ± 0·25° F, allow the sample to remain in the bath for thirty minutes, and make the indentation as before. The following further precautions are necessary in making indentations at this temperature :

(*a*) It is necessary that the sample shall be immersed for exactly thirty minutes, after which the indentations are made immediately. This necessity is due to the fact that many waxes undergo phase changes at this temperature. These changes may take up to an hour for completion. Thus if a 125/30 wax is tested after thirty minutes' immersion it will probably give a higher hardness than after, say, forty-five minutes' immersion.

(*b*) Care must be taken to apply the full load for exactly thirty seconds, because some waxes are relatively soft at this temperature and therefore the ball is continuously penetrating the wax, whereas in the case of most waxes at 60° F the impression is produced practically instantaneously when the full load is applied.

4. *Measurement of Diameter of Indentation.*

Place the sample on the base plate of a travelling microscope measuring to 0·002 cm and illuminate the surface of the specimen with a small electric lamp (say 6 v) suitably shielded by a reflector. Arrange the sample so that one of the indentations is below the microscope. Move the lamp until the concave surface of the impression reflects the light through the microscope and adjust until the periphery at one side of the concave surface is brightly reflecting the light. This will define the edge of one side of the impression sharply. Adjust the cross wire of the microscope to coincide with the brightly reflecting edge, and take the reading. Remove the light to the opposite side of the microscope so that the directly opposite edge is similarly illuminated and the cross wire adjusted at the diametrically opposite point. The difference between two readings gives the diameter of the impression. It may be noted that the ridge does not always show the same clear definition. The reflectivity of the concave surface of the impression appears to vary with different kinds of waxes and the perfection of the ridge around the impression also varies. But it is usually possible by suitable adjustment of the illumination to obtain a satisfactory reading. It is best to hold the hand lamp at an angle on the side of the indentation opposite to the periphery which is being measured.

It may be noted that it is somewhat easier to measure the diameters of the impressions of wax samples that have been removed from the moulds since the reflection of light from the internal surfaces of the mould tends to interfere with the sharpness of the measurement.

The mean of six readings is taken.

5. *Calculation of Results.*

From the mean diameter of the impression the hardness number is derived from the well known Brinell formula :

$$\text{Hardness Number} = \frac{P}{2\pi r(r - \sqrt{r^2 - D^2/4}} \text{ kg/sq. cm.}$$

where P = total weight = 6·5 kg.
r = radius of ball = 0·4775 cm.
D = diameter of impression in cm.

6. *Accuracy of Results.*

The mean probable percentage error may be taken as roughly ± 2 per cent of the Hardness Number.

II. Cone Hardness.

Up to the present, no routine test of cone hardness has been employed.

1. *Apparatus.*

Since the tip is relatively sharp, it is essential that the cone be contacted with the wax under conditions approximating to no load. Various devices have been satisfactorily employed :

(*a*) A movable housing in which the contacting is made with the axis of the cone horizontal to the sample face. The load is then applied by moving the housing so that the axis of the weighted cone becomes vertical.

(*b*) By carrying the weight of the cone, rod, and platform assembly on a spring. In this case a correction for the reaction of the spring must be made.

(*c*) Counterbalancing the weight of the cone and rod assembly and using an electrical contacting device.

The total weight of cone and rod assembly is 1·5 kg for a 60° cone. It is useful, however, to so design the apparatus that loads from 0 to, say, 5·0 kg can be employed.

So far, cones have been employed which are blunted at right angles to the axis of the cone so that the diameter of the tip is 0·04 cm (within fine-instrument-work tolerances).

An optical, or other scale, is attached to the rod carrying the cone, to read to 0·002 cm.

2. *Preparation of Sample.*

As for Ball Hardness.

3. *Production of Indentation.*

This is generally the same as for Ball Hardness.

Indentations are, however, made at any selected run of temperatures, the bath being maintained to within $\pm 0{\cdot}25°$ F of the best temperature.

For investigational work, the sample should be immersed in the bath not less than 1 hour before the test is made.

As before, six indentations are made.

4. *Measurement of Depth of Impression.*

This is read direct from the scale.

5. *Calculation of Results.*

From the mean depth of the six impressions the cone hardness is derived as

$$H_c = \frac{P}{\frac{1}{3}\pi h^2} \text{ in the case of a } 60° \text{ cone}$$

where P = applied load (usually 1·5 kg).
h = depth of penetration in cm.

6. *Accuracy.*

As for ball hardness.

Discussion.

The Chairman (Mr E. A. Evans): I think most chemists become accustomed to being told that a substance which they are handling and which they have handled in the past is not now what it was thought to be. So it has been very consoling to hear from a chemist that a substance which he has been investigating is, after all, what I thought it was many years ago. I felt tempted to use the phrase "deemed to be"; but when I was thinking of that phrase my thoughts went to the "*I.P. Review*" for March, in which there is a paper on "Engine Lubrication and the Law," by our very good friend Mr Biske, who describes what Mr Justice Cave thinks he thinks when he is thinking of the word "deemed." It is pleasant to know how to define something precisely in terms used by a High Court Judge. He said: "Generally speaking, when you talk of a thing being 'deemed' to be something, you do not mean to say that it is that which it is deemed to be. It is rather an admission that it is not what it is deemed to be and that, notwithstanding it is not that particular thing, nevertheless for the purpose of the Act it is deemed to be that thing." How perfectly simple and straightforward! Now we know precisely what we are talking about! I do feel that this sort of jargon used by lawyers is sometimes indulged in a little by chemists. A person asks "What is paraffin wax?" Some chemists, I do not include Mr Minchin, will go into a long explanation about all the normal paraffins and their neighbours. It is a little confusing when someone tells you at a later date that what you have accepted in the past is entirely wrong: it does upset many things which have been based upon it. For example, supposing someone carried out static-friction tests with great ability and precision, thinking he was using an *n*-paraffin, and it was found later that his results were a misrepresentation owing to the fact that there was 3 per cent of soft wax present; that would be disappointing. So it is pleasant to be told that, after all, the paraffin waxes are principally composed of crystals of *n*-paraffins, together with small amounts of soft waxes of the cyclic-paraffin type, which is what some of us supposed them to be.

A very wide field indeed has been covered in this paper, and I am quite sure that many are anxious to take part in the discussion and to thank Mr Minchin for what he has done.

DR C. M. CAWLEY : There is really relatively little in the scientific literature about petroleum wax, and this is at least partly due to the fact that it is a difficult subject. All the more credit is, therefore, due to Mr Minchin for presenting a paper packed with information, which I believe will be a valuable source of reference for many years to come.

The paper is very interesting to the Fuel Research Station in connexion with their work on the Fischer–Tropsch process—one of the major products of which is, or may be, paraffin wax, and it is therefore of interest to make a few comparisons of petroleum wax with Fischer–Tropsch wax.

The first point concerns the molecular-weight range of the two waxes. Mr Minchin has said that the commercial paraffin waxes cover the range C_{17} to C_{34}, and the ceresins and petrolatum waxes C_{34} to C_{60}. The Fischer–Tropsch waxes cover a more extended molecular-weight range, which moreover can be modified according to the catalyst and conditions used in the synthesis. Thus, in the medium-pressure process with a cobalt catalyst, the molecular-weight range of the waxes is C_{18} to C_{80}, and with an iron (Lurgi) catalyst is C_{18} to C_{150}. With a ruthenium catalyst at 200 atm the range is C_{18} to C_{1600}. The processes with the iron and ruthenium catalysts were only operated on a small scale in Germany, and the process to be operated in America will not produce any wax. The only process which has been operated on a commercial scale, therefore, is that using the cobalt catalyst, and it is the wax produced in this process which is the subject of the following remarks.

It appears that even the "cobalt" wax should provide a source of waxes of higher setting point than petroleum waxes, and it is in fact a fairly simple matter to separate from Fischer–Tropsch wax a fraction with a setting point of about 100°C. Is it true that C_{60} represents the wax of highest molecular weight which it is practicable to separate from petroleum? I ask this question because the statement had been made to him that petroleum could provide the same range of waxes as the Fischer–Tropsch process (cobalt catalyst) if these were required. Was this correct?

Referring to the statement made by Mr Minchin that of the commercial waxes, 96 to 97 per cent are normal paraffins and 3 to 4 per cent, the soft waxes, are non-normal paraffins. Fischer–Tropsch wax is generally regarded as consisting to a much greater extent than petroleum wax of *normal* paraffins. Thus, if Fischer–Tropsch wax is distilled, the residue is always a hard wax, and there is no tendency for it to become softer owing to the concentration of the higher-boiling soft waxes, as would happen with petroleum wax. Ruhrchemie have, however, stated that Fischer–Tropsch wax contains 10 to 20 per cent of *iso*-paraffins. There was an apparent discrepancy here, which perhaps Mr Minchin can clear up. It is evident that the *iso*paraffins in Fischer–Tropsch wax consist of long chains with very short side chains, perhaps no more than one methyl group to a molecule. Mr Minchin has not claimed that his substantially *n*-paraffins were wholly normal, and I think he might very well say that a wax consisting of perhaps thirty carbon atoms in a straight chain with a single methyl group in a side chain would be included in the fraction described as the mainly normal paraffins. If this were the case, could he say where he drew the dividing line? In other words, how much branching does the

molecule require to have before Mr Minchin will classify it with the soft waxes rather than the mainly *n*-paraffins?

In conclusion, I would refer to the ceresins and petrolatum waxes. Recently before this Institute an interesting account of polythene was given by Mr Richards, who described the influence of chain-branching on crystallization, and hence on the hardness and plasticity of polythenes. Mr Minchin has now painted the same sort of picture for waxes to account for their hardness and softness. I think that his hypothesis is most illuminating, but there is one point on which I ask for clarification. Mr Minchin has said that pure *n*-paraffins may readily range themselves with their long axes parallel, and hence give rise to a crystalline structure. In commercial wax, however, containing paraffins of varying chain length, short molecules range with long molecules in higgledy-piggledy fashion, so that the solidified wax consists of a conglomerate of micro-molecular zones of crystallinity and non-crystallinity. In the extreme case, therefore, one might expect a mixture of long and short molecules to give a plastic wax, and in fact Ruhrchemie did produce a Fischer–Tropsch plastic wax during the war by blending thirty parts of a hard wax with a melting point of 90° C with seventy parts of a soft wax with a melting point of 40° C. The product was to outward appearance a plastic wax, and this would seem to support Mr Minchin's thesis on solidification. Wax technologists had, however, been very scathing about this plastic wax produced by Ruhrchemie, which they declared was not a plastic wax at all. I understand that a true plastic wax usually contains a high proportion of non-normal paraffins of the same setting point as the normal paraffins, but it was not clear whether non-normals are essential to the property of plasticity. From Mr Minchin's hypothesis it would appear that this property should also be shown by a mixture of short and long normal chains. I would be glad to have Mr Minchin's views on the matter.

Mr G. F. Hazzard: I should like to take up his suggestion that perhaps the ball-hardness test is a short cut to the determination of oil content. We have had many discussions already on how to determine oil content. He has quoted figures showing a remarkable variation in hardness with oil contents ranging only up to 2 per cent. His results were obtained by adding an oil which is not closely defined in the paper. I would like to ask whether it is a wide-range oil, ranging from a liquid up to a solid hydrocarbon, or whether it is a closely cut fraction.

All of us, I think, are not really certain what is the oil in wax. We have all tried to obtain some, in order to put it back again. I feel that, if Mr Minchin could clarify that point, it might help us to see whether or not the oil content is so closely associated with the hardness as his findings indicate.

Mr W. J. Wilson: Having been associated with Mr Minchin's work from the outset I must express appreciation of the way in which he has handled the paper, and still more of the manner in which the work described has been carried out over a period of many years. When the work was started, some seventeen years ago, our knowledge of paraffin wax was considerably less than it is to-day, and the first necessity was to find some

test as a measuring stick whereby the qualities of waxes could be measured; I think Mr Minchin made a very happy choice when he decided to use the property of hardness. No one who has listened to the presentation of the paper can have failed to realize to what extent his findings have depended on that method, and I think he has afforded us an outstanding example of the value of such a new tool in research if it is handled as skilfully as he has handled it in this case. By means of that property, many other properties have been assessed and evaluated, so that a great deal of new knowledge has been revealed to us in Mr Minchin's paper. I should like to thank him for his excellent contribution.

Mr E. Thornton: I am particularly interested in Mr Wilson's remarks. I was one of the gang many years ago, and I would like to congratulate my friend Mr Minchin on the advance made from the "cookery" of those days to the newer chemistry of to-day. I was very much impressed by the similarity of the approach to this wax research to that which was put before us in the polyethylene research, and also in the Fischer–Tropsch work; and it would seem to me that the problems come still more closely together to-day. For instance, I note in a previous paper that the property of viscosity followed closely increasing molecular weight, whereas that of melting point showed this property tailing off to a maximum. I wonder whether more has been done than is given in the paper in using viscosity at the melting point as an indication of either straightness (as against cyclicity) or the actual molecular weight. Perhaps Mr Minchin will say whether it can be used.

Further, in regard to these settings, does the change in density give any indication of the changes which occur in the liquid form and persist into the solid? Has that been investigated, and does it throw light on these problems?

At the International Congress of Pure and Applied Chemistry, held in London last summer, a visitor from California said he had made a reassessment of all sorts of physical constants with relation to their measured maxima melting points, and so on. I wonder whether, if hardness were determined at a proportion of the absolute temperature and the setting temperature were at some distance from it, it might show a different relationship than if we used different temperatures, such as 60° and 80°. There may be something in that, and I put forward the suggestion without daring to pose as a wax expert.

Mr C. E. Mold: Perhaps I may make a few remarks, inasmuch as I am concerned more with the utilization of paraffin wax than are most of those who have taken part in the discussion so far. Frankly, I do not feel that I can ask questions; further, I feel that most of the work has not yet reached the stage at which Mr Minchin can provide the answers.

The sort of problem that arises in the practical use of wax, as in moulding, for example, is that of producing a strong article without serious technical difficulties. When wax was first used for making candles it was noticed that most of the waxes would produce candles which, after moulding, were structurally weak. We used to refer to the necessity for "closing" the crystals, and in the early days of wax candles that was done by adding

commercial stearic acid. The weakness was very closely associated with mottle development, and there is probably a great deal to be said for the Scott Harley and Lord hypothesis concerning the situation on reaching the transition temperature. There was the old habit of candle makers, when they had a wax that was liable to produce mottle, to put some wet cotton waste, or even a wet brick, into a pan of melted wax; the theory is that the evolution of water vapour de-aerated it. But the theory of Scott Harley and Lord does not seem to give the full explanation. If you put in 2½ per cent stearic acid you can perhaps suppress the transition point. On the other hand, when you come down to 0·1 per cent of Carnanba wax or even smaller quantities of polythene you can see the same effect taking place. Again, is it a question of the slowing down of the transition or of accelerating it?

I do not think the answers to these problems will easily be found, but work such as Mr Minchin has done may ultimately enable us to modify the molten properties of wax on scientific lines, instead of more or less empirically or by guess-work.

Dr A. S. C. Lawrence: I suppose that everyone present has been brought up in their organic chemistry upon the name "straight-chain" compounds. Everyone knows that the chain is a zigzag one in the solid crystalline state, but it is not yet realised sufficiently that the axis of the chain is straight in the crystalline chain only because of the restraint due to surrounding similarly orientated molecules. In the liquid or vapour state, in the absence of this restraint, the chain molecule is not straight; in fact, it has no definite shape—only a statistical one. The analogy of a worm is instructive: it has a length when straight, but if we observe it for 24 hours we should find that it spends most of the time in positions more or less curved and with a length from its nose to the tip of its tail less than the fully elongated length. This effective length may be anything from zero to the full straight-position length, but the latter is the least probable. The effective length which it has during the greatest part of the 24 hours is that distance between its ends which is achieved with the maximum number of different forms of curvature of its body. In chain molecules, this is due to free rotation about the C–C bonds and is quite different from a simple rotation of a straight-chain molecule about its long axis. If a chain molecule is surrounded by others shorter than itself, part of it is not under the restraint of the neighbours, and this part can behave like our worm, and will be a liquid while the remainder of the molecule may be straight-chain solid by reason of the packing restraint. This is a formal statement of Mr Minchin's hypothesis. This coiling is of paramount importance in macromolecules, but there is evidence that it occurs in molecules as short as those of the paraffin waxes in the liquid state: *e.g.*, the energy activation of viscous flow in the paraffin homologous series is a linear function of chain length only up to C_8 after which it falls off, which has been attributed to coiling setting in.

Dr W. M. Mazee: Mr Minchin has given a picture of commercial paraffin wax. I had an opportunity to examine pure normal $C_{21}H_{44}$ and a few other normal hydrocarbons which were synthesized. In the litera-

ture, Müller states that upon heating the normal $C_{21}H_{44}$ is gradually going to the hexagonal form, so that the rotation of the molecules about the long axis is complete before the melting point of the hydrocarbon is reached. But I think he has not had the pure substance. We found a very sharp transition point at about 3° C below the melting point, and a stable form above the transition point in which the rotation of the molecules about the long axis started gradually; as determined by X-ray investigation, the rotation was not yet complete at 1° C below the melting point.

The technique we used with which to investigate the position of the transition point, and which gave at the same time the heat of transition and of fusion, involved the use of a silver vessel completely filled with nickel gauze to give a uniform temperature distribution in the solid material. Then, in heating the substance and plotting temperature against time, there is first a rise of temperature, then at a very sharply defined point there is a horizontal part of the curve, which is the transition of the hydrocarbon, followed again by a rise of temperature, and then a very sharp melting until the material becomes liquid. In a mixture of two hydrocarbons of which the chain lengths are not too far apart—say the normal $C_{21}H_{44}$ and $C_{23}H_{48}$—the sharp melting disappears, there is a lowering of the transition point by about 5° or 6° C; at the same time the horizontal part in the transition curve disappears. The heat of transition is not actually measured at one temperature, but extends over a certain range of temperature. These hydrocarbons form a continuous range of mixed crystals. A commercial wax, which contains a whole range of normal paraffin waxes, say from $C_{21}H_{44}$ to $C_{36}H_{74}$, may show the following picture: the hydrocarbons having none too divergent chain lengths form a continuous range of mixed crystals, which in all cases will result in a lowering of the transition point. This may explain why at room temperature paraffin wax is always in the modification which is stable immediately below the melting point. Neither in this case is there a sharp transition point, but one must rather speak of a transition zone extending over a large temperature range. The heat of transition will then be distributed over the same temperature range. Therefore, the total heat of fusion measured in the case of a commercial wax will be lower than that of a pure normal hydrocarbon, the total heat of fusion of the latter consisting of a heat of transition and a heat of fusion of the modification stable immediately below the melting point.

MR V. L. SHATWELL: In Table II Mr Minchin indicates that the hardness reaches a maximum at round about 135° to 140° F, and then decreases with increasing molecular weight, and so on. But when we come to the petroleum ceresines, they are all very hard. Does that mean that there is some sort of irregularity in the hardness in relation to the molecular weight; does it go up and then down and then up again with increasing molecular weight?

Another point is the pronounced effect of the petroleum ceresines and to a less extent the petroleum waxes as modifiers of the crystallinity of the lower molecular weight paraffin waxes. They are "microcrystalline" in structure and very small quantities, such as 1 or 2 per cent, will confer this property on ordinary paraffin wax.

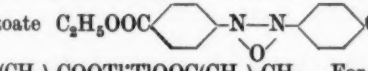
It seems extraordinary, if they are just straight-chain paraffins, that this should occur. Why is it that these higher-molecular-weight paraffins can effect the lower members so greatly, a property which apparently ceases when molecular weight falls below a certain figure. If it is a case of long chains interfering with shorter chains, why do not the middle members have a similar effect on the very low-molecular-weight paraffins?

We have found the cooling curve a very useful method of differentiating between the different types, and there is a characteristic difference between the curves given by recognized paraffin waxes, petroleum ceresines, and petrolatum waxes, which seems to indicate that there is some more fundamental difference than just molecular weight.

Mr C. G. Gray: I want to comment on the difficulties, which become obvious to anyone who has to work day in and day out with the solid hydrocarbons, of defining precisely what is meant by "solid" and by "liquid." Mr Minchin has introduced us to those difficulties by pointing out that in some hydrocarbon mixtures the situation can arise that a single *n*-paraffin molecule can in fact be solid at the end of the chain and liquid in the middle, or *vice versa*.

Another point of a similar nature which occured to me some time ago is that, in the case of a homogeneous paraffin, the situation arises that with crystallization the molecules range themselves parallel to each other and with the ends ranged along a plane. If you then heat the crystal so formed, I think there is evidence to indicate that the melting starts along the base plane on which the molecules are situated, and that over a temperature range the crystal is actually bound by liquid forces in one plane and by solid forces in a direction perpendicular to that plane. I know of no similar state of affairs in any other type of crystal. Has Mr Minchin come across a crystal which is liquid in one direction and solid in another?

Further, he pointed out that a peculiar result had been obtained in determining the hardness of paraffin-wax fractions, the effect being noticed that a sudden break in the hardness characteristics occured with a setting point of 58° to 60° C (*i.e.* about C_{26}); the hardness was determined at 60° F. I have suggested in a paper, with which Mr Minchin is familiar, that even normal paraffins in the range from C_{20} to C_{26} exist at room temperatures, not in the vertical opaque form, but a tilted opaque form, and the change on cooling is from the transparent form to the tilted, whereas above C_{24} it is from the transparent to the vertical opaque form. That change in crystalline habit at C_{24} to C_{26} may very well account for Mr Minchin's findings.

Dr A. S. C. Lawrence: Layer flow of the smectic liquid crystalline type is well defined in certain substances such as ethyl *p*-azoxybenzoate  and Thallous soaps $CH_3(CH_2)_nCOOTl$;$TlOOC(CH_2)_nCH_3$. For the lateral-plane adhesion, the presence of polar groups in the middle of the elongated molecule seems to be necessary, and this layer flow has never been observed in hydrocarbons.

Mr N. H. Ray: There is one small point which is not clear to me. I

should like to ask why it is necessary to use a fixed weight of sample in the hardness tests.

MR H. C. RAMPTON : With regard to the curves in Fig.1, would it be possible for these to be drawn on some boiling-point scale ? I realize the difficulties encountered when converting boiling points under vacuum, but it seems to me that at the moment you get a false impression ; the curves are wide apart and you cannot discover easily at which particular points changes occur in the nature of the distillates. I wondered whether it would be advantageous to draw curves on the boiling-point basis.

Another point which occurs to me is that there are other paraffin hydrocarbons within the gasoline range of higher melting points than the *n*-paraffins, *e.g.*, there is hexamethylene ethane with a melting point of 101°. Is it possible that some of the very highly branched structures which may exist in waxes have melting points considerably higher than the *n*-paraffins ? I do not know whether X-ray work has been done on these structures, but I make the suggestion, for I feel there may be something in it.

MR S. T. MINCHIN, replying to the discussion, said : I cannot hope to answer many of the questions adequately in the time at my disposal this evening, and probably I shall not be able to answer many of them adequately at any time ! But perhaps I may be able to expand some of my replies in writing.

Dealing first with the remarks of Dr Cawley concerning the Fischer-Tropsch waxes and the possibility of separating waxes above C_{60} from petroleum wax, so far as I am aware—and I am very much open to correction here—C_{60} should be taken as very approximately the limit of the *n*-paraffins that occur in crude petroleum. Therefore, I do not think it is likely that *n*-paraffins of a much higher molecular weight are likely to be separated from petroleum. I imagine, however, that when petroleum technologists have stated that hydrocarbon waxes of high molecular weight may be derived from petroleum, they have in mind synthetic processes similar to the Fischer–Tropsch.

Regarding the matter of chain branching raised by Dr Cawley, it should first be pointed out that the figures in the paper to which he refers concern commercial paraffin waxes. The figures quoted by Ruhrchemie refer to a mixture of substantially higher molecular weight. If a petroleum wax of equivalent molecular weight is compared with the Fischer–Tropsch product, there is little doubt that the same tests would show that the petroleum product contained more non-normal paraffins. Moreover, it has not yet been altogether made clear how the Ruhrchemie estimate was obtained although it was probably by the method of Gross and Gradde (*Oil and Kahle*, 1942, **16**, 410) which is based on an assessment by physical properties. I have not employed this method and am not therefore qualified to pass an opinion on its significance.

It is agreed that the " *n*-paraffin mixtures " described in the paper may well contain a wax consisting of perhaps thirty carbon atoms in a straight-chain with a single methyl group. I would certainly hesitate to offer an opinion where any dividing line should be drawn. At the moment, it appears not unreasonable to adopt a purely empirical method and consider

the concentrates that can be isolated by the distillation and crystallization methods from time to time described as consisting of non-normal concentrates, and the balance (apart from rejected oil or oily fractions) as normal paraffin concentrates. Therefore, I cannot yet answer the question Dr Cawley asks, for I do not know how much chain branching has to exist before the molecule is recovered as a non-normal.

As to whether blends of short and long chain paraffins produce a "plastic" wax, as claimed by Ruhrchemie, really rests on how the term plastic is defined. Strictly speaking I would agree that the Ruhrchemie "Plastic wax" mixture was plastic in the sense that it may be continuously and permanently deformed without rupture during the application of a force which exceeds the yield value of the material. On the other hand, petroleum technologists usually mean that in addition to this there must be a toughness and hardness before the material is commercially useful. This requirement appeared to necessitate the presence of high-molecular-weight non-normal hydrocarbons. In this latter sense, the criticisms that Ruhrchemie wax was not "plastic" were justified.

In reply to Mr Hazzard's query on the oil employed in deriving the oil content–hardness curve; it was assumed that the oil normally present in the refined wax was the "oil" rejected as filtrate after the last-priming stage as refined after the finishing treatment applied to the wax (it being assumed that the finishing treatment was mainly directed to "refining" the traces of oil left in the wax). Therefore the filtrate oil from the last stage of pressing was subjected to a heavy treatment adjusted to correspond to the calculated treatment it received when present in the wax. It was therefore a wide-range oil (lube base) and had a cloud point of 38° F.

I would suggest that no one definition can cover what is meant by "oil." Primarily, I think, "oil" is the portion of the hydrocarbon mixture that is liquid at the temperature on which our attention happens to be focussed.

I agree with Mr Thornton on the matter of viscosity. It may be pointed out that Gross and Grodde attempted to assess what they called the ring value or cyclicity of paraffin waxes. They apparently take the view that a cyclic body has a higher viscosity than either a pure *n*-paraffin or a branch-chain paraffin of the same molecular weight, and therefore a viscosity measurement may be used to assess cyclicity. There is, however, a great deal of work still to be undertaken on this subject, and I agree that some examination of the viscosities of the pure compounds is called for first.

Seyer and collaborators, in the paper which I have quoted, are of the opinion that their observations on densities would lead to the belief that there was a certain amount of ranging above the setting point.

With regard to assessing the hardness at what one might term, for want of a better term, the "corresponding states," I think Mr Thornton has made an interesting suggestion. It has received some consideration in the past, but the idea has not yet had an opportunity to be developed.

As to Mr Mold's remarks on the evolution of air at the transition point, I would point out that there is here being discussed a theory propounded by other investigators. I think that many of the waxes with which Mr Mold is concerned would exhibit no transition. Moreover, it is difficult to see how air could come out, in these cases, due to transition effect. That

air comes out is generally agreed, but the mechanism is probably not due to transition in the case of most commercial waxes.

Mr Mold raises the difficult question of the effect of modifiers; namely, why small percentages of certain wax-like materials have such a profound effect on the crystallinity of the wax to which they are added. I am unaware of any satisfactory answer yet given to this phenomenon. It may be suggested that such modifiers cause the formation of extensive "micromolecular micelles" in the wax, but it is then difficult to understand why so small a quantity of modifier produces so large an effect. Probably the question is bound up with questions of random distribution and that what is required to solve the problem is a more mathematical study.

I am very glad that Dr Lawrence has raised the matter of "kinked carbon chains"; I hesitated to raise the matter myself because I find the mathematics exceedingly difficult to follow and my incursion into this field was immediately damned by mathematical physicists. I have wondered—and I am almost asking Dr Lawrence for information—whether that kinking and twisting of the chain, due to rotation around the carbon atom, which I believe is due to thermo-kinetic bombardment, does take place to any very great extent at temperatures so near the setting point. If Stewart and Warren found there are pockets of the pure *n*-paraffins of similiar straight-chain length which are ranged throughout the length of the chain, is it because the chain is not long enough to kink, in the *n*-paraffins, or because kinking does not take place?

Dr Lawrence: I think that in these experiments probably only 10 per cent at most of the material will give the lattice pattern. There is the question of the interdependence of viscosity. But experiments have shown that, when we get to about C_{10} or C_{12} the energy of activation of viscous flow begins to fall away from the straight line, and it continues to divert more and more as we go up. It does seem that there is something very queer in the way of the alteration of the shape of the molecule setting in extremely early.

I admit that this is a virgin field, and we should like to know more about it.

Mr Minchin: I am very glad indeed to see Dr Mazee here, and to renew his acquaintance after so many years; and I hope to have an opportunity of discussing the more interesting experiments he describes.

It is agreed that, where transition occurs in commercial waxes, it must take place over a temperature range; and the theory advanced by Dr Mazee is attractive. In many cases, however, the evidence advanced in the paper appears to suggest that no, or very little, transition occurs.

Then Mr Shatwell referred to the curve showing a maximum hardness, at a setting point somewhere about 58° C, of 135 to 140, and then decreasing. He asked whether, in the case of the harder waxes, there is a second minimum on the curve. I do not know, but I strongly suspect there must be. So far it has not been possible to resolve the range of ceresins into a range of fractions similar to the commercial paraffins. The opinion is hazarded, however, that there may be a minimum hardness occurring about the position of C_{36}, because after C_{36}, as Mr Gray has pointed out, the transition and setting point coincide.

The effects of modifiers I have dealt with already in reply to Mr Mold. To this I would add that I think that there must be a minimum chain length before a molecule is capable of exhibiting micromolecular micelles.

I am very glad that Mr Gray contributed to the discussion, and I am delighted to see him here. As to the problem of melting in one plane but not in another, that has been dealt with by Dr Lawrence more adequately than I could hope to do.

As to the forms that can exist over the ranges at which break hardness occurs, I agree that Mr Gray has furnished an alternative explanation to the one I have advanced in the paper. In both cases, however, the development of the break is postulated as due to polymorphism.

On Mr Ray's question as to why a fixed weight of sample is used in the hardness tests, the answer is that it was to ensure cooling rates which were substantially the same throughout; smaller samples cool more rapidly.

Agreement is expressed with the point made by Mr Rampton, that it would perhaps have been better to have plotted the various densities against the boiling-point scale, and I thank him for pointing this out.

The last point, that maybe there are other hydrocarbons having higher setting points than the *n*-paraffins, has been considered. All that can be said is that so far no evidence of it has been obtained. It is, however, a possibility which must always be considered.

Vote of Thanks.

THE CHAIRMAN: I am sure that the charm and directness with which Mr Minchin presented his paper to us has filled us with confidence in his ability to speak on the subject and has made it very pleasant to listen to him. We are indeed very grateful to you, Mr Minchin, for this very long paper. The preparation of such a document with all its attendant experimental work is a very big task. The text is continuous and full of valuable material, and is indeed most comprehensive.

On behalf of the Institute of Petroleum, I do wish to thank you very heartily for having prepared it, for coming here to present it, and for answering the questions so ably.

(The vote of thanks to Mr Minchin was accorded with enthusiasm.)

DR A. S. C. LAWRENCE in a written contribution, said: After examining the exhibits and from experience of other impure waxes, I suggest that great care should be taken in drawing conclusions from hardness tests. Hardness depends upon the physical properties of each crystal in a solid and upon the forces between the crystals. The latter especially varies with the size and crystal habit of the crystals. Suppose we take a pure wax hydrocarbon and add to it a few per cent of an oil which is adsorbed on the solid wax crystals. Its presence must depress the setting point. When solid begins to separate, the size of the crystals may be reduced by adsorption of the oily impurity and, as we know, their habit will tend to change from thin plates to needles. When cold, the crystals will be separated by a thin film of oil—not air as will a pure wax—which will give them their semi-transparent look. The hardness of a lump will now

be much less because the oil plasticizes or lubricates the slip of the crystals past one another in flow.

I suggest that this picture explains much of Mr Minchin's results without recourse to posulation of departure from normal paraffinicity, a theory which as speakers pointed out was based on evidence of most dubious authenticity.

I may add that I have made up mixtures of wax and anti-freeze oil as a successful de-icing preparation for H.M. ships in the Arctic. In these the wax separated as solid above 0° C and further cooling increased consistency only by the increase of the viscosity of the wax-free oil. The wax acted as a " sponge " providing a surface layer of oil sufficient to give easy detachment of ice and at the same time, will stand weathering by gales up to 150 knots. The optimum proportions found were three parts of hard petrolatum and one of anti-freeze lubricating oil.

MR MINCHIN in reply, wrote: Dr Lawrence's suggestion that the appearance of the non-normal concentrates may be explained on the basis that they are mixtures of normal paraffins and an oil is considered less satisfactory than the one advanced in the paper because :—

1. In the case of purified *n*-paraffins (as a pure *n*-paraffin) the development of capacity is in the opposite direction from the one suggested by Dr Lawrence. That is to say the wax is more transparent in the higher temperature ranges than in the lower. It is generally agreed that this is because the high-temperature-stable form is transparent, and the low-temperature-stable form is not. Thus a wax can exist as a transparent form in the absence of oil.

2. There is no evidence known to me suggesting that any hydrocarbon oil is adsorbed on crystals of *n*-paraffin or *n*-paraffin mixtures in sufficient quantity to give the effect suggested by Dr Lawrence. Microscopic examination reveals oil as existing as droplets on a crystal face and not spread over it.

3. Either Dr Lawrence is concerned with my postulate of departure from *n*-paraffinicity, or he is not. If he is, then the example of de-icing preparations is probably irrelevant, since the bulk of published opinion would, I think, agree that petrolatums are not mainly normal paraffins.

If Dr Lawrence means that non-normal paraffins adsorb oil in conformation, then I think I would agree; but in this case I fail to see the point of his argument.

4. It is agreed that all the waxes discussed in the paper were impure in the sense that they were not chemical individually. Whether care was taken over the inferences made is clearly for people other than the author to decide. But suggestions such as these add no more proof to the contention made by Dr Lawrence that the non-normal concentrates were in fact mixtures of an oil which was adsorbed on *n*-paraffin crystals than my suggestion that the methods of preparation lead to an inference that they are in fact concentrates of non-normals. Moreover, Buchler and Graves and Feonis, Cawley, and Hinderman, using similar methods of preparation also consider these concentrates as mainly non-normal in composition. Dr Lawrence either suggests that all these workers are mistaken, or that the samples described by me differ in some way from concentrates similarly

obtained by other workers. Dr Lawrence may be correct in this: but it does not seem unreasonable to state that the evidence which he advances in support of the suggestion is not particularly convincing.

I have re-read the remarks made by other speakers, and am at a loss to explain Dr Lawrence's statement that the characterisation of concentrates as "non-normal" was pointed out by speakers to be of more dubious authenticity.

MR C. F. MCCUE in a written contribution, said: Mr Minchin is to be congratulated on presenting a paper which, besides recording the results of some very useful investigations, will undoubtedly stimulate considerable thought and discussion among other workers in this field. There are, however, one or two aspects on which I should like him to elaborate.

The first concerns the measurement of latent heats of fusion and transition. It seems to me that the total heat evolved by 1 g of wax cooling from a temperature $t1$ (above its melting point) to room temperature, $t2$, is made up of three components: (i) the heat lost due to its drop in temperature, (ii) the latent heat of fusion, and (iii) the latent heat of transition. That is to say

$$t_1 H t_2 = S(t_1 - t_2) + L_F + L_T$$

Where S is the average specific heat of the wax over the range t_1 to t_2 and L_F, L_T are, respectively, the latent heats of fusion and transition.

Mr Minchin refers to the latent heat of fusion "measured down to normal room temperatures," and I am not clear whether he means t_1Ht_2 or $L_F + L_T$. I assume the latter.

When working with pure n-paraffins these three components are fairly well defined, but in the case of commercial waxes it is virtually impossible to disentangle them. Garner, Van Bibber, and King[7] in their work on n-paraffins record the "heat of crystallization to the α form" and to the β form; these values correspond to L_F and $L_F + L_T$. Kolvoort[19] states that "for pure n-$C_{24}H_{50}$ 21·0 cal/g was found at 47·4° C; the latent heat of fusion at 50·8° C was 60·8 cal/g." It would seem that 60·8 cal/g is intended to represent L_F, but it is more compatible with the values obtained by the previous workers for $L_F + L_T$, and Mr Minchin gives it this latter significance (Table III).

Table V cites some results obtained by Parks and Todd, who it would appear were endeavouring to measure L_F. Their method was that of mixtures—heating the sample in a steel capsule to various temperatures, dropping it into water at 25° C and observing the rise in temperature. I quote from their paper—"By the use of various upper temperatures—for instance, one somewhat below the melting point of the sample, a second slightly above and a third perhaps 30° or 40° above the melting point—adequate data could be obtained for the calculation of the heat fusion of the substance as well as of its interval specific heats in both the crystalline and liquid states." Provided that the first of these three temperatures was above the transition point, the quantity measured would be L_F. Mr. Minchin, however, assumes it to be $L_F + L_T$ and then uses the apparent lowness of the results as evidence of impurity of the samples.

Sullivan and his co-workers[25] use the term "heat of crystallization" to

refer to the heat of solution of wax in gas oil, but in Table IV their results are recorded as " latent heat of fusion (to room temperature)."

Obviously a closely defined nomenclature is necessary in order to avoid confusion in the interpretation of results.

Turning to the relative hardness of the two crystal forms, I am very uncertain as to the significance of the statement that " the high-temperature stable form is softer than the low at the same temperature."

The fact that the transition point of pure *n*-paraffins is sharply defined suggests that the transition $\alpha \rightleftharpoons \beta$ is fairly complete and if any α form should be present at a temperature below the transition point it would be expected to pass into the β form on standing. Thus measurement of the hardness of the two forms at the same temperature implies that one form is in a metastable condition and any results obtained on it would probably be anomalous. From Figs. 13 and 15 it is apparent that the hardness of the α form varies much less with temperature than does the β form, but to extrapolate that part of the curve due to the α form does not seem justifiable.

Mr Minchin would, no doubt, be the first to agree that considerably more work is necessary on these subjects before really sound conclusions can be formed.

MR MINCHIN in reply to Mr C. H. McCue: By the latent heat " measured down to normal room temperatures " is meant $L_F + L_T$ as Mr McCue suggests.

It was taken that the value given by Kalvoort [19] as 60·8 cal/g referred to $L_F + L_T$, although I agree that the paper quoted would suggest that it is L_F, as Mr McCue points out this brings it in line with other published results.

Provided the first temperature " somewhat below the melting point of the sample " was above the transition point in the paper quoted (Parks and Todd) [28] I agree that the value found was L_F. But, for very-highly purified waxes the transition point approaches the setting or melting point. I therefore assumed that the value of latent heat found was for $L_F + L_T$; if it is not, then the results are even more inexplicable when compared with work on the synthetic *n*-paraffins.

The point made regarding Sullivan and his co-workers is agreed. A note should have been inserted in the table to this effect.

It is agreed that in the case of pure synthetic *n*-paraffins the transition $\alpha \rightleftharpoons \beta$ is probably instantaneous and fairly complete. And it is further agreed that, in this instance, the measurement of hardness of the two forms at the same temperature implies one form is in a metastable condition. In the case of *n*-paraffin mixtures and commercial waxes, however, the same state of affairs does not appear to apply. If the evidence given in the paper is taken as justifying the assumption that in these cases transition is never complete, but that what would be the high-temperature stable form (in the case of a pure *n*-paraffin) can exist in a stable condition in such mixtures at temperatures below the transition ranges, then it may be granted that it is justifiable to consider the general qualitative inference from extrapolation, and it may also be granted that the phrase " the high-temperature stable form is softer than the low at the same temperature "

may have a physical significance. This is the line taken in the paper. If, however, the evidence and explanation given in the paper is rejected, then I would agree that the terms I have employed would be meaningless and confusing."

I would certainly be the first to agree that the paper I have presented does no more than state some of the problems surrounding the behaviour of wax in the solid state. I agree also that the conclusions I have given cannot be complete and probably are not always sound. I stated in the paper, that one of my main objects was to stimulate thought and discussion on this exceedingly difficult subject.

ALLOWANCE FOR LOSSES DUE TO EXIT, ENTRANCE, AND FITTINGS FOR A GAS FLOWING IN A PIPE UNDER HIGH PRESSURE DROP.

By E. S. L. Beale (Fellow) and P. Docksey (Associate Member).

The formulæ usually applied to flow calculations for a gas flowing isothermally in a pipe either take account of friction only, or, if including the effect of kinetic energy changes (as is usual when dealing with a case where pressure drop is high compared with the absolute pressure) only cover those in the pipe itself, thus giving the pressure difference between two points both located within the length of the pipe. Little account is taken of entrance and exit losses, or of the correct method of allowing for fittings, *i.e.*, by first evaluating the loss in terms of the number of velocity heads. The object of this note is to consider the application of these various corrections, especially for the case of flow through a pipe connecting two large vessels where only the overall pressure difference is known.

It has been demonstrated [1] that the most satisfactory method of expressing losses due to fittings and changes of section (including entrance to the pipe from a large tank), is in terms of velocity heads. At the same time it is usually more convenient to include the losses in the actual flow equation in terms of the equivalent additional length of straight pipe, and it is easily demonstrated that the relation between S, the number of velocity heads due to the fitting,* and the equivalent increase in length expressed as a number of pipe diameters, N, is :

$$N \times D = \frac{S}{8(R/\rho v^2)}$$

where $(R/\rho v^2)$ is the friction factor and D is the pipe diameter.

The conception of allowing for the pressure loss due to a fitting in terms of velocity heads is easily grasped in the case of liquid flow, since the velocity-head pressure is independent of the static pressure. Thus, if the pressure loss due to a fitting is S velocity heads, the actual loss in pressure will be the same whether the fitting is placed near the entrance of the pipe where the absolute pressure is high, or near the exit, where it is low. In the case of a gas flowing under conditions of high pressure drop, the velocity-head pressure is increasing along the pipe due to expansion of the gas as the pressure falls, and hence the loss in pressure due to a fitting with S velocity heads is less if it is placed near the inlet than if it is near the exit. In other words, if the loss in pressure due to a fitting is to be calculated directly from the known loss in terms of velocity heads, it is necessary to know whereabouts

* The list of symbols is given at the end of the paper. The units used throughout are self-consistent on the conventional system *e.g.*, Foot-Mass Pound-Second, except for pressures which are expressed in the type of unit always used in engineering, namely Force Pounds (per square foot) instead of Poundals (per square foot). For this purpose the numerical conversion factor g_c is introduced. The units applicable to the C.G.S. system are shown in the list of symbols.

it is located in the pipe before allowance can be made for it correctly. This difficulty is easily resolved, however, if the number of velocity heads is converted to additional length. The additional length due to a fitting with a pressure loss equal to S velocity heads is ND, and if the physical operation were carried out of removing the fitting, and replacing it by a length ND of pipe, the flow and pressure-drop conditions would be undisturbed, and the compensation for the fitting would be complete, independent of whereabouts in the length of line the incision is made.

This point can also be demonstrated by considering the equation used to convert a loss of S velocity heads into the equivalent length of line N (expressed in pipe diameters) :—

$$N = \frac{S}{8(R/\rho v^2)}$$

where $(R/\rho v^2)$, the friction factor, is a function of the Reynolds Number and for a perfect gas flowing isothermally, the latter is independant of the pressure, as may be readily seen if it is written in the form $Re = \frac{GD}{\eta}$. (Note that for a perfect gas η, the absolute viscosity, is independent of pressure.) Thus, for a perfect gas flowing isothermally in a pipe the Reynolds Number, and hence the friction factor, is constant over the whole length, and the additional length to which a fitting is equivalent will also be constant. Departure from ideality of the gas will not seriously affect this conclusion, except in the comparatively rare cases where the compressibility factor is large, and flow in the pipe is near the critical region.

This method of making the correct allowance for loss due to fittings in the pipe with gas flowing under high pressure drop can be used also for the entrance loss, that is, the frictional loss at the entrance to the pipe due to turbulence, etc., caused by a square-shaped inlet, etc.

The meaning of the term " exit loss " requires a little explanaton, and this is as follows. In the case of a liquid, the " exit loss," expressed in terms of pressure drop, is the pressure necessary to supply the kinetic energy carried away with the liquid at the exit from the pipe. There will be a drop in static pressure at the entrance to the pipe, even with an ideally rounded entry, equal to the velocity-head pressure of the liquid in the pipe; but this pressure drop may be largely recovered if the exit from the pipe is suitably shaped, that is with a gradually tapering enlarger or diffuser. Alternatively, the drop in static pressure may be completely lost if the exit is square. Although this drop in pressure occurs at the entrance to the pipe, its recovery or otherwise depends on the conditions at the exit, and hence the loss is referred to as the " exit loss." For fully turbulent flow, where the velocity may be considered uniform across the cross-section of the pipe, the pressure drop due to this exit loss at a square exit is simply equal to the velocity-head pressure or dynamic pressure in the pipe.

Now considering the more complicated case of a gas flowing with a high pressure drop, the calculation of the pressure loss due to kinetic energy is complicated by the expansion of gas as it flows down the pipe, with a corresponding increase in kinetic energy. Thus, in the case of a pipe with a square exit, the pressure drop due to exit loss is not equal to the velocity-head pressure at the inlet, but must in addition allow for the further increase

in kinetic energy due to expansion down the pipe. It might at first be thought that the allowance for exit loss should simply be a pressure drop equal to the velocity-head pressure at the exit of the pipe. This is not so, because the pressure drop is not directly proportional to the increase in kinetic energy with a compressible fluid.

The correct value for the exit loss applicable to a gas flowing under high pressure drop can be derived as follows :—

Consider a pipe in which gas is flowing isothermally under turbulent conditions, with a rounded entrance from a large vessel at absolute pressure P_1, and with a square exit into a large vessel at pressure P_2. The absolute pressures just inside the pipe at either end are P_3 and P_4, as shown in Fig. 1 where the corresponding linear velocities and densities are also indicated.

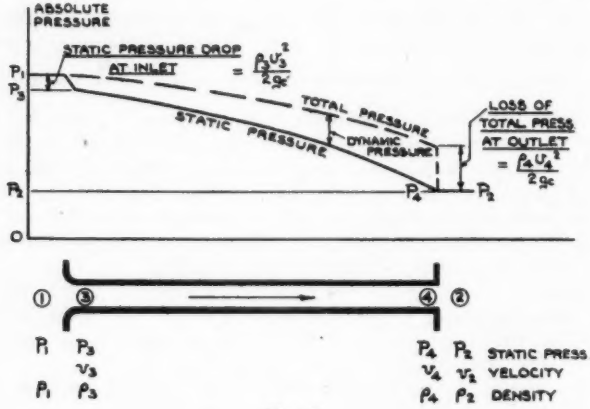


FIG. 1.

DIAGRAM OF PRESSURES, ETC.

Notice first that the static pressure, P_2, just outside the exit end of the pipe, is identical with P_4, just inside the pipe, as are also $v_2\rho_2$ and $v_4\rho_4$.

Then an application of Bernoulli's Theorem gives [2]

$$\frac{P_3^2 - P_4^2}{2P_3} = \left[8(R/\rho v^2)\frac{L}{D} + 2\log_e\frac{P_3}{P_4}\right]\frac{\rho_3 v_3^2}{2g_c} \quad . \quad . \quad (1)$$

This is the formula usually given, but it neglects the drop in pressure at the inlet to the pipe. Note that the first term inside the bracket corresponds to the effect of friction, while the second corresponds to the increase in kinetic energy between the two points P_3 and P_4, both of which are inside the pipe.

Substituting P_2 for P_4 and rearranging :—

$$P_3 - P_2 = \left[8(R/\rho v^2)\frac{L}{D} + 2\log_e\frac{P_3}{P_2}\right]\frac{2P_3}{P_3 + P_2}\cdot\frac{\rho_3 v_3^2}{2g_c} \quad . \quad (2)$$

Now, since a well-rounded entrance is postulated, it may be assumed that the normal flowing velocity distribution is established immediately on

entry into the pipe, and that, since the flow is turbulent, the velocity is uniform over the cross-section. We then have :—

$$P_1 - P_3 = \frac{\rho_3 v_3^2}{2g_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Combining (2) and (3)

$$\begin{aligned} P_1 - P_3 + P_3 - P_2 &= P_1 - P_2 \\ &= \left[8(R/\rho v^2)\frac{L}{D} + 2\log_e \frac{P_3}{P_2}\right]\frac{2P_3}{P_3 + P_2} \cdot \frac{\rho_3 v_3^2}{2g_c} + \frac{\rho_3 v_3^2}{2g_c} \\ &= \left[8(R/\rho v^2)\frac{L}{D} + 2\log_e \frac{P_3}{P_2} + \frac{1}{2}\left(1 + \frac{P_2}{P_3}\right)\right]\frac{2P_3}{P_3 + P_2}\frac{\rho_3 v_3^2}{2g_c} \quad (4) \end{aligned}$$

By the gas laws $P_3\rho_3 v_3^2 = P_2\rho_2 v_2^2$,
and hence (4) becomes

$$P_1 - P_2 = \left[8(R/\rho v^2)\frac{L}{D} + 2\log_e \frac{P_3}{P_2} + \frac{1}{2}\left(1 + \frac{P_2}{P_3}\right)\right]\frac{2P_2}{P_3 + P_2} \cdot \frac{\rho_2 v_2^2}{2g_c} \quad (5)$$

Equation (5) is strictly correct, but its solution involves a knowledge of P_3, the pressure inside the pipe at the entrance. Since only P_1 and P_2 are known, P_3 can only be obtained by approximation. In many cases of practical importance, P_3 is nearly equal to P_1, and as a rough approximation we may substitute the latter for the former in equation (5). Doing this, we obtain the following approximate formula :—

$$P_1 - P_2 \simeq \left[8(R/\rho v^2)\frac{L}{D} + 2\log_e \frac{P_1}{P_2} + \frac{1}{2}\left(1 + \frac{P_2}{P_1}\right)\right]\frac{2P_2}{P_1 + P_2}\frac{\rho_2 v_2^2}{2g_c} \quad (6)$$

The term $\frac{1}{2}\left(1 + \frac{P_2}{P_1}\right)$ inside the bracket corresponds to the drop in static pressure at the inlet. If this is neglected we obtain equation (6*a*), the one usually given, but which should only be applied to the flow between two points in the pipe and not to the case of flow between two large vessels.

$$P_1 - P_2 = \left[8(R/\rho v^2)\frac{L}{D} + 2\log_e \frac{P_1}{P_2}\right]\frac{2P_2}{P_1 + P_2} \cdot \frac{\rho_2 v_2^2}{2g_c} \quad . \quad (6a)$$

We now have three possible means of calculating the flow between two vessels in which the pressures are P_1 and P_2, namely, by the strictly accurate equation (5); by the more convenient, but approximate form of this, equation (6); and finally by equation (6*a*), the one usually applied, but which neglects the drop in static pressure at the inlet to the pipe. A series of calculations made under strictly comparable conditions using the three equations will reveal, first the degree of error involved in using the usual method, equation (6*a*); and secondly the inaccuracy involved in the approximate form of the equation, equation (6). Such a comparison is given in the following table, which shows values of $\frac{\rho_2 v_2^2}{2g_c}\Big/P_2$, the ratio of the velocity-head pressure at the exit to the absolute pressure there, calculated for a range of values of P_1/P_2 of approximately 1·1 to 10·0, and values of

$8(R/\rho v^2)\frac{L}{D}$ of 2 to 100. These latter values correspond to values of $\frac{L}{D} = 100$, 200, 500, 1,000, and 5,000 at a friction factor, $(R/\rho v^2) = 0{\cdot}0025$.

The columns in the table are as follows :—

(1) Values of P_1/P_2.

(2) Corresponding values of P_3/P_2.

(3) Values of $8(R/\rho v^2)\frac{L}{D}$.

(4) Values of $\frac{\rho_2 v_2^2}{2g_c}\Big/P_2$ calculated from equation (6*a*), *i.e.*, neglecting the inlet static pressure drop.

(5) Values of $\frac{\rho_2 v_2^2}{2g_c}\Big/P_2$ calculated from the exact equation (5).

(6) Values of $\frac{\rho_2 v_2^2}{2g_c}\Big/P_2$ calculated from the approximate equation (6).

(7) Values of $\frac{\rho_2 v_2^2}{2g_c}\Big/P_2$ calculated from a revised form of equation (6), empirically adjusted to minimise the errors due to the approximation. This is equation (7) given later.

P_1/P_3.	P_3/P_2.	$8(R/\rho v^2)\frac{L}{D}$.	Values of $\frac{\rho_2 v_2^2}{2g_c}\Big/P_2$.			
			Neglecting inlet : equation (6*a*).	Exact. : equation (5).	Approx. : equation (6).	Approx. : equation (7).
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1·144	1·1	2	0·06786	0·04793	0·04802	0·0476
1·123	1·1	4	0·03079	0·02506	0·02518	0·02507
1·109	1·1	10	0·01129	0·01030	0·01033	0·01031
2·221	2	2	0·5470	0·4430	0·4552	0·4390
2·139	2	4	0·3239	0·2785	0·2859	0·2791
2·066	2	10	0·1428	0·1317	0·1340	0·1326
2·035	2	20	0·0734	0·0701	0·0710	0·0703
5·332	5	4	1·869	1·6623	1·7272	1·657
5·182	5	10	0·974	0·907	0·930	0·908
5·103	5	20	0·537	0·516	0·524	0·519
10·20	10	20	2·085	2·011	2·045	2·008
10·05	10	100	0·477	0·473	0·475	0·472

Since, on any horizontal line in the table, P_2 may be regarded as constant, the differences in the values of $\frac{\rho_2 v_2^2}{2g_c}\Big/P_2$ obtained by the various methods of calculation can be looked on as differences in values of v_2^2, *i.e.*, as a measure of the error in the calculated rate of flow.

It will be apparent that reasonable accuracy is attained by the use of formula (6), and that the errors which would be obtained if the inlet static pressure drop were neglected (demonstrated by comparing columns (4) and

(5) in the table) are greatly reduced. However, at the higher values of P_1/P_2 it is evident that the use of the approximate equation (6) introduces an error about half that obtained by neglecting the inlet static pressure drop. This error can be further reduced by modifying equation (6) by increasing the co-efficient of the log term from 2 to 2·2, giving :—

$$P_1 - P_2 = \left[8(R/\rho v^2)\frac{L}{D} + 2{\cdot}2 \log_e \frac{P_1}{P_2} + \frac{1}{2}\left(1 + \frac{P_2}{P_1}\right)\right] \frac{2P_2}{P_1 + P_2} \cdot \frac{\rho_2 v_2^2}{2g_c} \quad (7)$$

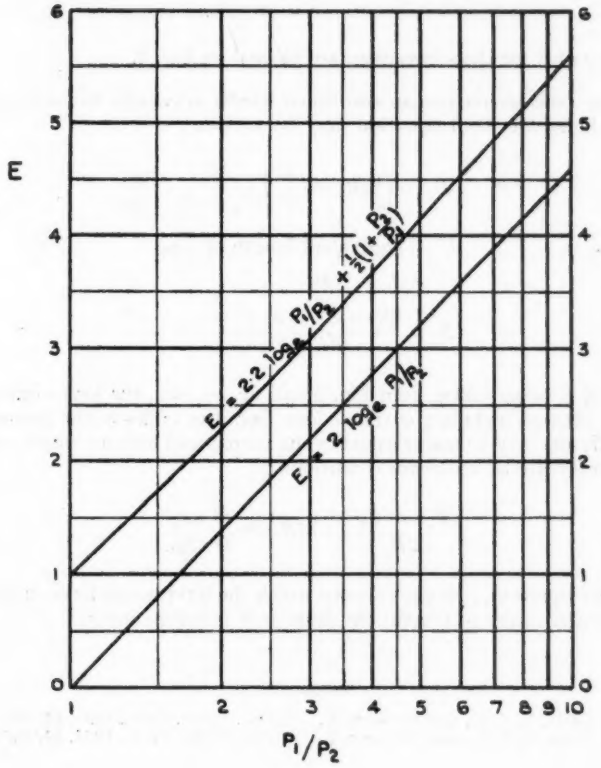


FIG. 2.
EXIT LOSS, E.

The values of $\frac{\rho_2 v_2^2}{2g_c} \Big/ P_2$ obtained from this equation are given in column (7) of the table, and comparing these with the exact values in column (5) we can see that good agreement is obtained.

Equation (7) can be written as follows :—

$$P_1 - P_2 = \left[8(R/\rho v^2)\frac{L}{D} + E\right] \frac{2P_2}{P_1 + P_2} \cdot \frac{\rho_2 v_2^2}{2g_c} \quad . \quad . \quad (8)$$

In this equation the values of E for the two types of application are as follows:—

Value of E.	Application.
$E = 2{\cdot}2 \log_{10} \frac{P_1}{P_2} + \frac{1}{2}\left(1 + \frac{P_2}{P_1}\right)$	Flow between two large vessels in which the pressures are P_1 and P_2.
$E = 2 \log_{10} \frac{P_1}{P_2}$	Flow between two points in a pipe at which pressures are P_1 and P_2.

Values of E for these two cases are plotted on Fig. 2.

E may be converted to an additional length in exactly the same way as S, and hence the final equation may be written:—

$$P_1 - P_2 = \left[8(R/\rho v^2)\frac{L'}{D}\right]\frac{2P_2}{P_1 + P_2} \cdot \frac{\rho_2 v_2^2}{2g_c} \quad . \quad . \quad . \quad (9)$$

Where:— L' = equivalent length of pipe

$$= L + ND$$

$$N = \frac{(E + S_1 + S_2 \ldots)}{8(R/\rho v^2)}$$

values of E being taken from Fig. 2 and S_1, S_2, etc., the losses due to the various fittings, including entrance loss, from the tables in the literature.

Finally (9) may be transformed to the more usual form in which velocity and density are at upstream conditions

$$\frac{P_1^2 - P_2^2}{2P_1} = 8(R/\rho v^2)\frac{L'}{D}\frac{\rho_1 v_1^2}{2g_c} \quad . \quad . \quad . \quad . \quad (10)$$

In this equation, v_1 is the velocity which the fluid would have *in* the pipe if the density were to remain the same as it is before entry.

References.

[1] Beale, E. S. L., and Docksey, P. *J. Inst. Petrol. Tech.*, 1932, **18**, 607.
[2] Beale, E. S. L., and Docksey, P. *J. Inst. Petrol. Tech.*, 1928, **14**, 236.

List of Symbols.

D = Pipe diameter (cm).
E = Allowance for kinetic energy (no. of velocity heads).
g_c = Numerical constant equal to standard gravitational acceleration (non-dimensional = 981).
G = Mass rate of flow (g/sec).
L = Length of pipe measured along centre line with fittings in position (cm).
L' = Effective length of pipe = $L + ND$ (cm).
N = Number of pipe diameters.
P_1, P_2, P_3, P_4 = Absolute pressure of gas at points 1, 2, 3, 4 (g/sq. cm).

$(R/\rho v^2)$ = Friction factor * (non-dimensional).
S = Number of velocity heads.
v_2, v_3, v_4 = Velocity of flow at points 2, 3, 4 (cm/sec).
v_1 = Velocity which the fluid would have in the pipe if the density were to remain the same as it is before entry (cm/sec).
ρ_1, ρ_2, ρ_3, ρ_4 = Density of gas at points 1, 2, 3, 4 (g/cc).
η = Absolute viscosity of gas (poises).

* The expression $(R/\rho v^2)$ has been retained as the friction factor in order to avoid the anomalies which sometimes arise if the symbol f is used. There is, therefore, no need for the reader to be bothered with exact definitions of R, ρ, and v, but for more detailed discussion see reference (2).

THE INSTITUTE OF PETROLEUM.

THIRTY-FOURTH ANNUAL GENERAL MEETING.

THE Thirty-Fourth Annual General Meeting of the Institute of Petroleum was held at Manson House, 26, Portland Place, London, W.1, on Wednesday, April 9, 1947, Mr G. H. Coxon (Chairman of Council) presiding in the absence of the President.

THE SECRETARY (Mr F. H. Coe) read the notice convening the meeting.

The Minutes of the Thirty-Third Annual General Meeting, held on March 13, 1946, and of the Adjourned Meeting held on January 8, 1947, were taken as read and signed.

ANNUAL REPORT.

The Annual Report for 1946 of the Council, having been circulated, was taken as read. On the motion of Mr F. L. Garton, seconded by Dr E. R. Redgrove, it was unanimously adopted.

OFFICERS FOR 1947–48.

President.

THE CHAIRMAN : It is now my pleasure to announce that the Council has unanimously re-nominated Sir Andrew Agnew, C.B.E., as President for the Session 1947–48.

On the motion of Mr T. Dewhurst, seconded by Lt.-Col. S. J. M. Auld, the meeting unanimously re-elected Sir Andrew Agnew.

Vice-Presidents.

THE CHAIRMAN : It is my privilege to announce that the under-mentioned have been nominated Vice-Presidents for the Session 1947–48 :—

G. H. Coxon.
E. A. Evans.
A. C. Hartley.
J. S. Jackson.
J. A. Oriel.
H. C. Tett.

On the motion of the Chairman, seconded by Dr E. B. Evans, the above named were unanimously elected.

Hon. Treasurer.

The Council recommended the appointment of Mr G. H. Coxon as Hon. Treasurer for 1947.

LT.-COL. S. J. M. AULD : I should like to have the opportunity to pay tribute to the excellent work which Mr Coxon has done in this and other respects on behalf of this Institute. With great pleasure I propose his election.

DR A. E. DUNSTAN: I take pleasure in seconding the proposition, and in supporting the tribute to Mr Coxon.

The resolution was carried unanimously; and Mr Coxon expressed his thanks for the kind remarks made.

Hon. Secretary.

The Council recommended the appointment of Mr C. Chilvers as Hon. Secretary for 1947.

On the motion of Dr W. E. J. Broom, seconded by Mr R. I. Lewis, the meeting unanimously elected Mr Chilvers.

Election to Council.

THE CHAIRMAN: I have to announce that eight vacancies exist on the Council. The following Members of Council retire but are eligible for re-election :—

E. J. Dunstan.
H. Hyams.
J. S. Parker.
E. R. Redgrove.
R. R. Tweed.

and three nominations have been received in favour of :—

A. T. Beazley.
Dr F. Morton.
H. de Wilde.

In consequence, no ballot is necessary, and I announce that the gentlemen named are hereby elected.

Ex-Officio Members of Council.

THE CHAIRMAN: In accordance with the By-laws, it is necessary for us to elect ex-Officio Members of Council, and I propose that the following be so elected.

H. A. Ruffell A. Featherstone	Northern Branch
W. R. Guy	Scottish Branch
R. B. Southall	South Wales Branch
V. Biske H. E. F. Pracy	Stanlow Branch

The above-named members were duly elected.

New Members.

THE CHAIRMAN ordered that a list of Fellows, Members, Associate Members, and Students elected or transferred during 1946 be laid on the table.

ADJOURNMENT.

THE CHAIRMAN: It is my duty now, as Chairman of this meeting and as Chairman of the Finance Committee, to ask for a proposition that this

meeting be adjourned until the audited accounts are completed, or until such time as the Council may decide, of which due notice will be given.

We have not been able to get the accounts through yet; but we felt that we should get this business of the Annual General Meeting well ahead, even though we have not the completed accounts.

(On the motion of Dr A. E. Dunstan, seconded by Mr T. Dewhurst, the meeting resolved that the proceedings be adjourned until the accounts were ready for presentation.)

Vote of Thanks.

Mr T. Dewhurst: I would like to propose a vote of thanks to our Chairman; and would mention that he has just completed a very heavy year of work as Chairman of the Council.

Mr C. A. P. Southwell seconded, and the motion was carried with acclamation.

The Chairman: Thank you very much. The past year has not been a very hard year; but there have been difficult problems to settle, and there will be more and more in the future. The post-war period is even more difficult than I had thought it would be. No matter what we try to do, we find ourselves up against snags, and however much one tries to follow a programme, one just cannot do it.

One thing which disappoints me more than anything else is that we have not been able to secure additional accommodation. We must expand. We have a programme for securing additional accommodation in this building, but we could extend beyond that. I think there is tremendous scope for this Institute.

(The business of the Annual General Meeting was adjourned.)

ADJOURNED THIRTY-FOURTH ANNUAL GENERAL MEETING.

The Thirty-Fourth Annual General Meeting was resumed on June 9, 1948, when the Chair was taken by Mr G. H. Coxon (Hon. Treasurer). The notice convening the meeting was read by the General Secretary (Mr F. H. Coe).

The Chairman: We regret that the presentation of the accounts for 1946 has been so long delayed, but that is entirely due to the fact that the audited accounts have only recently been received.

I would like to direct your attention to the Revenue Account, the principal item of interest being that for the first time since 1938 a deficit is shown. That deficit is £768, but the Finance Committee foresaw a long time ago that, with the end of the war, we should have to face a considerable expansion of our work and prepared for it by building up a reserve.

During the year there was a noticeable increase in membership, and this is reflected in the amount of subscriptions received.

It will be noted that throughout the Revenue Account there is evidence of the greater activities of the Institute during 1946—on the income side by increases in receipts from sales of publications, and on the expenses side by increased administration costs due mainly to the appointment of the

Publications and Technical Secretaries needed to handle the additional work. Likewise, the cost of publications was higher on account of increased circulation and printing charges.

The Benevolent Fund is dealt with in a separate account. You will see that the Fund received two very useful contributions during 1946; a legacy of £500 was paid by the Executors of the late James Gillespie, and the Oil Industries Club donated 30 guineas in that year. These contributions have been duly acknowledged by the Institute.

We are dealing only with the accounts for 1946. But I think I might mention that in the 1947 accounts, which we are hoping to get very soon, we shall show another big loss. However, the Council and the Finance Committee are now taking full advantage of the new By-law to create Member-Companies; letters are going out shortly to innumerable companies in Britain, inviting them to co-operate in the work of the Institute by becoming Member-Companies.

There being no questions, the CHAIRMAN formally moved :—

> " That the Accounts and Balance Sheet as audited by the Institute's Auditors, and showing the position of the Institute's affairs as at 31st December, 1946, be approved and are hereby accepted."

PROFESSOR J. S. S. BRAME : I have very much pleasure in seconding the proposition from the Chair for the adoption of the Accounts and Balance Sheet for 1946.

The resolution was carried unanimously and the business of the meeting concluded.

REPORT OF COUNCIL FOR 1946.

ALTHOUGH conditions have been difficult, the many activities of the Institute have continued to expand during 1946.

MEMBERSHIP.

During the year 203 members and students were elected, the details of the membership as at December, 1946, being shown in the following table :—

	Total Dec. 31, 1945.	Changes during 1946. New.	Transferred to.	Resigned.	Deceased.	Transferred from.	+ or −.	Total Dec. 31, 1946.
Hon. Fellows	1	1	1	—	—	—	+ 2	3
Hon. Members	11	—	—	—	—	—	—	11
Fellows	459	17	10	4	3	1	+ 19	478
Members	648	57	10	16	4	5	+ 42	690
Assoc. Members	634	75	10	10	1	12	+ 62	696
Students	161	53	—	1	—	13	+ 39	200
Totals	1914	203	31	31	8	31	+164	2078

The total membership stands at 2078, but this figure is subject to review as it includes members with whom contact has been lost during the war. Special efforts are being made to get into touch with these members.

The Council regret to record the deaths of the following members :—

	Date elected.	Class of membership.
C. T. Bell	1938	Member
F. E. Cherry	1920	Fellow
E. H. Cunningham-Craig	1913	Fellow
H. C. S. Fothergill	1936	Member
Campbell M. Hunter	1919	Fellow
A. F. Strickland	1914	Assoc. Member
William Sutton	1913	Member
J. F. Taylor	1929	Member

Mr E. H. Cunningham-Craig was one of the Founder Members, and Mr William Sutton was an Original Member of the Institute.

Branches and Students' Section.

The branches continue to flourish, and interesting programmes of papers and meetings have been held in Great Britain and overseas. The Scottish Branch has been revived successfully.

The Birmingham Branch of the Students' Section has continued its meetings during the year.

The Council is encouraging the revival of the London Branch of the Section. Mr N. E. F. Hitchcock, the former Hon. Secretary of the Branch, is working in close co-operation with the Branches Committee in this connexion.

Publications.

The high standard of the *Journal* has been maintained. There have been increases over 1945 both in the Transactions and Abstracts Sections, the latter containing 1476 items.

A list of the papers read before the meetings of the Institute and subsequently published in the *Journal* is given below :—

1946.	Subject.	Author.
Jan. 9	"The Production of *iso*Hexane and *iso*-Heptane by Super-Fractionation."	S. F. Birch, P. Docksey, and J. H. Dove.
Feb. 13	"Petroleum in Wartime." (Presidential Address).	F. H. Garner.
Mar. 13	"The Development of Fluid Catalytic Cracking."	J. F. Walter.
Mar. 27	"The First Cadman Memorial Lecture."	Sir William Fraser.
Apr. 9	"The Sludge Test for Transformer Oils."	C. H. Barton.
	"A Review of the Mechanism of the Oxidation of Liquid Hydrocarbons."	P. George and A. Robertson.
	"Some Developments in the Refining of Transformer Oil."	J. C. Wood-Mallock.
	"Survey of B.E.I.R.A. Work on Transformer Oil."	P. W. L. Gossling and A. C. Michie.
	"Effect of Water Temperature on the Sludge Test."	P. W. L. Gossling and J. Romney.
	"Oxidation Tests for Transformer Oil."	A. A. Pollitt.
	"Oxidation and Anti-Oxidation."	E. A. Evans.
May 8	"The Geology of the Guayaquil Estuary, Ecuador."	G. Sheppard.

1946.	Subject.	Author.
June 12	"The Application of Variance Analysis to Some Problems of Petroleum Technology."	H. M. Davies.
Oct. 16	"The Lubrication of Pre-Selective Gearboxes."	A. T. Wilford.
Nov. 12	"Viscometry of Hydrocarbon Soap Systems."	F. H. Garner, A. H. Nissan, and G. F. Wood.
Dec. 11	Symposium on Oil Fires:	
	"Fires and Explosions at Oil Installations."	E. P. Lancashire.
	"Experiments on Rate of Foam Application."	N. O. Clarke, E. Thornton, and J. A. Lewis.
	"Behaviour of Oils Burning in Open Reservoirs and Effects of Air Agitation."	J. H. Burgoyne and L. L. Katan.

The Seventh Edition of "Standard Methods for Testing Petroleum and Its Products" was issued early in the year and preparations for the Eighth Edition are well in hand.

"Modern Petroleum Technology," which appeared towards the end of the year, has been well received and this volume is considered to fill a long-felt want in the general literature of petroleum technology.

The "Institute of Petroleum Electrical Code" was issued in booklet form, and this has received some complimentary reviews.

Much work has been done towards the issue of a Quinquennial Review of Petroleum Technology for the years 1941–45 to bring the valuable series of annual reviews up to date. It is hoped it will be published shortly.

The necessary steps were taken during the year to produce a second monthly journal under the title *The Institute of Petroleum Review*, the first issue of which appeared early in January 1947. This is intended to broaden the scope of the publications and to cover papers of general interest.

The Council received with regret the resignation of Dr A. E. Dunstan as Honorary Editor. They placed on record the great debt which the Institute owed to Dr Dunstan for his invaluable services in this connexion over a period of twenty-five years.

Standardization.

The work of the Standardization Committee has continued to expand during the year. There were, at the end of the year, forty-nine Sub-Committees, Panels and working groups, the majority of which have met many times throughout the year.

Many existing methods have been revised and new methods standardized. Close co-operation has been maintained with the A.S.T.M.

The Council desires to record its appreciation of the generous assistance of the petroleum industry in making available both members of their staff and laboratory facilities, without which the work of the Standardization Committee would be impossible.

"Standard Methods" are now accepted on a world-wide basis and the preparation of this annual publication is regarded as one of the most important functions of the Institute.

Research.

The Hydrocarbon Research Project is now in its third year of operation, and much valuable spectrographic data and data on chemical synthesis and analysis await publication. This highly specialized work is carried out at the Universities and elsewhere under the ægis of the Institute, and is financed by the subscribers to this particular project.

Education.

The Council has been concerned about the lack of an accepted standard of proficiency for junior members in the various branches of petroleum technology. A special Committee has been studying this problem, and in association with the City and Guilds of London Institute, considerable progress has been made with the preparation of a syllabus covering a five-years course in petroleum technology.

Library.

During the war years the library of the Institute was, through force of circumstances, inaccessible. Arrangements were made during the year to transfer the library to the Institute's present premises, and the original facilities for consulting and borrowing books are again available to members. It is hoped to extend the range of books and literature available and to provide an improved library service. To this end a librarian has been appointed and enquiries from members will be welcomed.

Finance.

The Council regrets that it has not been possible to complete the 1946 accounts in time for presentation at the Annual General Meeting.

Preliminary figures, which at the moment are being audited, indicate that there will be a deficit for the year, principally due to the higher administrative costs of the increasing work which has been accomplished during the year.

The Finance Committee are giving careful consideration to ways and means of meeting this deficit and also the further provision of funds to meet the increased costs anticipated for 1947.

The Finance Committee will issue a full report as soon as the accounts are complete.

Council and Officers.

Sir Andrew Agnew, C.B.E., was unanimously elected by the Council as President for the Session 1947–47 and G. H. Coxon was elected as Chairman of Council.

Messrs G. H. Coxon, E. A. Evans, A. C. Hartley, V. C. Illing, J. S. Jackson, and J. A. Oriel were elected as Vice-Presidents, and the following were elected as Members of Council as the result of a ballot of members: C. Chilvers, E. B. Evans, F. L. Garton, C. A. P. Southwell, H. C. Tett, A. Beeby Thompson, and C. W. Wood.

The Council received with great regret the resignation of Mr Arthur W. Eastlake, who had been Honorary Secretary of the Institute for thirty-two years. As an expression of appreciation for his services, the Council elected Mr Eastlake an Honorary Fellow of the Institute.

Auditors.

The Council recommends the re-appointment of Messrs Price, Waterhouse & Co. as auditors.

General.

Throughout the year a Committee of Council has been engaged on the revision of the By-laws. These are now in the hands of the solicitors, and a Special General Meeting will be called in due course to adopt the By-laws in their revised form.

The secretarial staff of the Institute has been strengthened during the year by the appointment of Mr Peter Kerr as Technical Secretary, with responsibility for all of the Standardization work, and Mr George Sell as Publications Secretary. The whole question of the staff establishment necessary to meet the expanding activities of the Institute is under review by the House Committee.

The Council wishes to express its thanks to the many members of Committees, panels, and working groups, and to the staff of the Institute for their invaluable services throughout the year.

By Order of the Council.
C. Chilvers, Hon. Secretary.

THE INSTITU

(A Company limited by Guara

BALANCE SHEET

	£	s.	d.	£	s.	d.
Capital of the Institute under Bye-Laws, Section 6, Paragraphs 14 and 15 :—						
Life Membership Fund—						
As at 31st December, 1945				899	4	0
Entrance and Transfer Fees—	£	s.	d.			
As at 31st December, 1945	4287	16	9			
Received during year—						
Entrance Fees	233	2	0			
Transfer Fees	19	19	0			
				4540	17	9
Profit on Sale of Investments—						
As at 31st December, 1945				351	10	11
Donations—						
As at 31st December, 1945				326	5	0
					6117	17 8
T. C. J. Burgess Prize Fund :—						
As at 31st December, 1945					5	0 0
(Cadman Memorial Fund)						
War Contingencies Reserve :—						
As at 31st December, 1945				1985	17	8
Less Transferred to Office and Library Furniture				283	16	9
					1702	0 11
Members' Subscriptions Received in Advance					222	13 2
Journal Subscriptions Received in Advance					415	8 3
Sundry Creditors, General Account					1573	4 0
World Petroleum Congress					260	5 0
Revenue Account :—						
Balance as at 31st December, 1945				6728	10	10
Less Deficit for year as per separate statement				768	5	11
					5960	4 11
(Research Fund)						
(Surplus)						
					£16,256	13 11

Approved by Council :
E. A. EVANS, President.
G. H. COXON, Hon. Treasurer.

AUDITOR

We report to the Members of THE INSTITUTE OF PETROLEUM that we have examined the abo
we have required. We are of the opinion that such Balance Sheet is properly drawn up so as
according to the best of our information and the explanations given to us, and as shown by t

3, FREDERICK'S PLACE,
OLD JEWRY, LONDON, E.C. 2.
8th April, 1948.

PETROLEUM.

not having a Share Capital.)

31ST DECEMBER, 1946.

								1945
			£	s.	d.	£	s.	d.	£
estments :—									
n Account of Capital, at cost—									
£461 12 0	3%	Conversion Stock, 1948/53	491	12	6				
525 0 0	3%	Savings Bonds, 1955/65	525	0	0				
500 0 0	3%	Defence Bonds	500	0	0				
867 8 6	2¾%	Bristol Corporation Redeemable Stock, 1955/65	845	17	7				
150 0 0	3%	Smethwick Corporation Redeemable Stock, 1956/58	151	4	9				
150 0 0	3%	Luton Corporation Redeemable Stock, 1958	151	6	7				
806 8 3	3%	Manchester Corporation Redeemable Consolidated Stock, 1958	845	17	7				
600 0 0	3%	Bristol Corporation Redeemable Stock, 1958/63	597	7	3				
664 6 6	3%	London County Consolidated Stock, 1920	481	10	6				
400 0 0	3%	Metropolitan Water Board "A" Stock, 1963	346	10	7				
150 0 0	5%	Wandsworth and District Gas Co. Debenture Stock	154	8	6				
125 0 0	5%	Great Western Railway Co. Consolidated Preference Stock	105	4	9				
		(Market Value at 31st December, 1946, £5743.)	5196	0	7				*5196*
		sh awaiting Investment on Deposit with Post Office Savings Bank	921	17	1				
						6117	17	8	*669*
n Account of Revenue, at cost—									
£790 8 3	3%	Conversion Stock, 1948/53	842	8	0				
500 0 0	3%	Defence Bonds	500	0	0				
475 0 0	3%	Savings Bonds, 1955/65	475	0	0				
2000 0 0	3%	Savings Bonds, 1960/70	2000	0	0				
336 5 10	3%	Conversion Stock, 1948/53	357	14	8				
		(Market Value at 31st December, 1946, £4357.)				4175	2	8	*4175*
		Cadman Memorial Fund)							*2809*
		ice and Library Furniture (excluding Presentations) :—							
		s at 31st December, 1945	163	1	5				*171*
		dditions during year	121	15	4				*10*
			284	16	9				*181*
		ess Transferred from War Contingencies Reserve	283	16	9				*18*
						1	0	0	*163*
		rary Books (excluding Presentations) :—							
		s at 31st December, 1945				—			
		bscriptions in Arrear :—							
		ot Valued				—			
		ndry Debtors				1222	3	4	*980*
		h at Bank on Current Account and in Hand				2099	8	3	*2664*
		h on Deposit with Post Office Savings Bank :—							
		eneral Account	2380	17	0				*2553*
		Vorld Petroleum Congress Account	260	5	0				*254*
						2641	2	0	
						£16,256	13	11	*£19,463*

EPORT.

he abo ance Sheet with the books of the Institute and have obtained all the information and explanations so as t ibit a true and correct view of the state of the Institute's affairs as at 31st December, 1946, n by th s of the Institute.

PRICE, WATERHOUSE & Co.,
Chartered Accountants.
Auditors

THE INSTITUTE

REVENUE ACCOUNT FOR THE

	£	s.	d.	£	s.	d.	1945 £
To **Administration Expenses :—**							
Staff Salaries and National Insurance	3399	17	8				1792
Printing and Stationery	409	0	4				206
General Postages	281	6	7				199
Telephone, Cables, Telegrams, and Travelling Expenses	66	15	9				46
				4157	0	4	
„ **Establishment Charges :—**							
Rent, less amounts recovered	374	19	4				375
Cleaning, Lighting, and Lift Expenses	211	13	3				208
(Depreciation)							18
				586	12	7	
„ **Publications :—**							
Journal Publication Expenses	3322	13	9				2356
Abstractors' Fees	194	19	3				186
Postage on Journals	239	7	3				185
Standard Methods Publication Expenses	537	19	3				639
Modern Petroleum Technology Publication Expenses	829	7	2				
Cost of other Publications	285	4	9				24
(Tables for Measurement of Oil)							891
				5409	11	5	
„ **Meetings :—**							
Hire of Hall, Pre-prints, Reporting, etc.				255	7	10	168
„ **Professional Fees :—**							5
Auditors' Fee				105	0	0	42
„ **Students' Scholarships and Prizes**				110	10	0	83
„ **Library Expenditure**				29	8	8	74
„ **Branches and Sections :—**							
Students' Section (Birmingham)	10	0	0				10
Stanlow Branch	36	12	0				69
Northern Branch	90	13	6				45
South Wales Branch	20	15	6				38
Scottish Branch	53	6	6				
Trinidad Branch	20	0	0				
				231	7	6	
„ **Sundry Expenses**				309	9	9	178
„ **(Surplus)**							1570
				£11,194	8	1	£9407

OF PETROLEUM.

YEAR ENDED 31ST DECEMBER, 1946.

	£	s.	d.	1945 £
By Subscriptions for 1946 received	4391	11	0	3889
" Special Subscription	20	0	0	20
" Subscriptions in Arrear, received during year	269	6	6	238
" Sale of Publications and Advertisements	5376	6	5	4903
" Interest and Dividends (Gross)	368	18	3	357
" Balance, being deficit for year, carried to Balance Sheet	768	5	11	
	£11,194	8	1	£9407

CADMAN MEMORIAL FUND.

INCOME AND EXPENDITURE ACCOUNT FOR THE PERIOD ENDED 31ST DECEMBER, 1946.

	£	s.	d.	£	s.	d.
To Balance as at 31st December, 1946 :—						
Cash at Bank on Current Account	83	17	10			
£2730 3% Savings Bonds, 1965/75 (Market Value 31st December, 1946, £3023)	2730	0	0			
Income Tax recoverable	76	10	9			
				2890	8	7
				£2890	8	7

	£	s.	d.
By Balance as at 31st December, 1945	2808	10	7
„ Interest received during the year and tax recoverable	81	18	0
	£2890	8	7

We have examined the above Income and Expenditure Account with the books and vouchers of the Fund, and find it to be in accordance therewith. We have verified the cash with Bankers to be in accordance with the balance on 31st December, 1946.

3, FREDERICK'S PLACE,
OLD JEWRY, LONDON, E.C. 2.
8th April, 1948.

PRICE, WATERHOUSE & Co.,
Chartered Accountants.
Auditors.

HYDROCARBON RESEARCH GROUP.

INCOME AND EXPENDITURE ACCOUNT FOR THE PERIOD ENDED 31ST DECEMBER, 1946.

	£	s.	d.	£	s.	d.
To Grants :—						
University of Cambridge	1875	0	0			
University of Oxford	1625	0	0			
University of Birmingham	886	14	1			
Bedford College	1250	0	0			
				5636	14	1
„ Honoraria				525	0	0
„ General Expenses				171	12	8
„ Balance as at 31st December, 1946				4780	0	10
				£11,113	7	7

	£	s.	d.
By Balance as at 31st December, 1945	5263	7	7
„ Contributions received from Members of the Group during the year	5850	0	0
	£11,113	7	7

We have examined the above Income and Expenditure Account with the books and vouchers of the Fund, and find it to be in accordance therewith. We have verified the cash with Bankers to be in accordance with the balance on 31st December, 1946.

3, FREDERICK'S PLACE,
OLD JEWRY, LONDON, E.C. 2.

PRICE, WATERHOUSE & Co.,
Chartered Accountants.

We have examined the above Income and Expenditure Account with the books and vouchers of the Fund, and find it to be in accordance therewith. We have verified the cash with Bankers to be in accordance with the balance on 31st December, 1946.

3, Frederick's Place,
Old Jewry, London, E.C. 2.

Price, Waterhouse & Co.,
Chartered Accountants.

BENEVOLENT FUND.

Receipts and Payments Account for Year ended 31st December, 1946.

Receipts.

	£ s. d.	£ s. d.	*1945* £
Balance on 1st January, 1946		1504 8 6	*1321*
Receipts during 1946 :—			
Subscriptions and Donations	739 17 0		*131*
Interest and Tax recoverable	41 6 9		*52*
		781 3 9	
		£2285 12 3	*£1504*

Payments.

	£ s. d.	*1945* £
Benevolent Fund :—		
Grants in Aid	—	
Balance on 31st December, 1946 *	2285 12 3	*1504*
	£2285 12 3	*£1504*

* The Balance on 31st December, 1946, was held as follows :—

	£ s. d.
Cash at Bank on Current Account	875 14 3
£850 0 0 3% Defence Bonds at cost †	850 0 0
£600 0 0 3% Local Loans at cost †	528 17 0
Income Tax recoverable	31 1 0
	£2285 12 3

† (Market Value at 31st December, 1946, £1453.)

We have examined the above Receipts and Payments Account with the books and vouchers of the Fund and find it to be in accordance therewith. We have verified the Investments and the Balances with Bankers and The Institute of Petroleum comprising the Balance on 31st December, 1946.

3, Frederick's Place,
Old Jewry, London, E.C. 2.
8th April, 1948.

Price, Waterhouse & Co.,
Chartered Accountants.
Auditors.

LIST OF DONORS AND SUBSCRIBERS TO THE BENEVOLENT FUND DURING 1946.

Adams, A. C.
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ERRATA.

"TANK CALIBRATION"

Page 304, Section A. 1, para (g), sub-para (i), line 3. *For* "0·1 ft" *read* "0·01 ft."

OBITUARY.

EVE NEYMAN-PILAT.

THE prominent Polish scientist and petroleum technologist, Dr Eve Neyman-Pilat, died suddenly on November 24, 1946, in Wroclaw (Breslau), Poland.

Eve Neyman-Pilat survived her husband, the well-known petroleum chemist, Prof Dr Stanislaw Pilat, F.Inst.Pet., by several years only. He was one of the first Poles to be executed by the Gestapo soon after the Germans invaded the country in September 1939.

Eve Neyman-Pilat was born in Lwów (Lemberg) in 1909. She studied chemistry at the Technical University in her native town and graduated there in 1932. In the following years she worked as lecturer and then professor's assistant in the Departments of Inorganic Chemistry, Physical Chemistry, and Petroleum Technology, in succession, showing even then an uncommon aptitude for scientific research.

In 1935 she married Stanislaw Pilat, under whose guidance she had worked in her student and lecturing days. This extraordinarily gifted couple tackled together many outstanding scientific problems of petroleum chemistry.

In 1937 Eve Neyman-Pilat obtained her doctor's degree at the University of Lwów, and then spent some time working with Professor Waterman in Delft. Together with her distinguished husband she took part in all the important international gatherings of chemists and petroleum technologists which were convened in the course of those years.

In 1937 the couple toured the U.S.A. and studied the various problems affecting the American oil industry.

During the German occupation of Lwów, Eve Neyman-Pilat temporarily suspended her activities in petroleum technology and worked in a pharmaceutical research laboratory. In 1944, after the occupation of Lwów by Soviet troops, she was recalled to the Department of Petroleum Technology at the Technical University of that city and resumed her interrupted scientific career. Later in 1944 Eve Neyman-Pilat moved to Kraków and was appointed Head of the Chemical Department of the Polish Petroleum Institute.

In 1945 Eve Neyman-Pilat was appointed Professor of Petroleum Technology at the newly founded Polish University of Wroclaw (Breslau). In this capacity she devoted herself with untiring energy to the transformation of the former " Kaiser Wilhelm Institut für Kohleforschung " in Breslau into laboratories for petroleum technology. Shortly after the assumption of her new duties she died suddenly, at the beginning of a very distinguished scientific career.

Despite her early death, Eve Neyman-Pilat has enriched petroleum chemistry by some very important work. She published some twenty-five scientific papers in British, American, Polish, Russian, and German scientific and technical periodicals, which give ample proof of the depth of knowledge and versatility of this remarkable young woman.

Eve Neyman-Pilat was elected a Member of the Institute of Petroleum in 1939.

Her scientific work covered many fields of petroleum chemistry. Amongst papers which Eve Neyman-Pilat published in British and American periodicals, the following are the most important :—

" Sulphonic Acids from Petroleum." *Industr. Engng Chem.*, 1934, **26**, 395
" Heat of Solution of Natural Gas Associated with Petroleum Oils." *Oil Gas J.*, 25.4.35, **33** (49).
" The Chemical Constituents of Paraffin-Base Lubricating Oils." *J. Inst. Petr. Techn.*, 1937, **23**, 669.
" Properties of Synthetic Lubricating Oils." *Industr. Engng Chem.*, 1941, **33**, 1382.

All those who have come into contact with that distinguished young scientist in Britain as well as in other countries, will remember her for her striking personality, her numerous gifts, and pleasant nature.

H. B.